IN THE UNITED STATES DISTRICT COURT
FOR THE DISTRICT OF DELAWARE

MOLECULAR REBAR DESIGN,	§	
LLC AND BLACK DIAMOND	§	
STRUCTURES, LLC,	§	
	§	
Plaintiffs,	§	C.A. No.
	§	
v.	§	
	§	JURY DEMAND
LG CHEM, LTD., LG ENERGY	§	
SOLUTION, LTD., LG ENERGY	§	
SOLUTION MICHIGAN, INC., AND	§	
LG ELECTRONICS, INC.,	§	
	§	
Defendants.	§	

ORIGINAL COMPLAINT FOR PATENT INFRINGEMENT

NATURE OF ACTION

1. Plaintiffs Molecular Rebar Design, LLC and Black Diamond Structures, LLC (collectively, "Plaintiffs") file this Complaint for patent infringement under 35 U.S.C. § 271 against LG Chem, Ltd., LG Energy Solution, Ltd., LG Energy Solution Michigan, Inc., and LG Electronics, Inc. (collectively, "Defendants") and allege as follows:

OVERVIEW

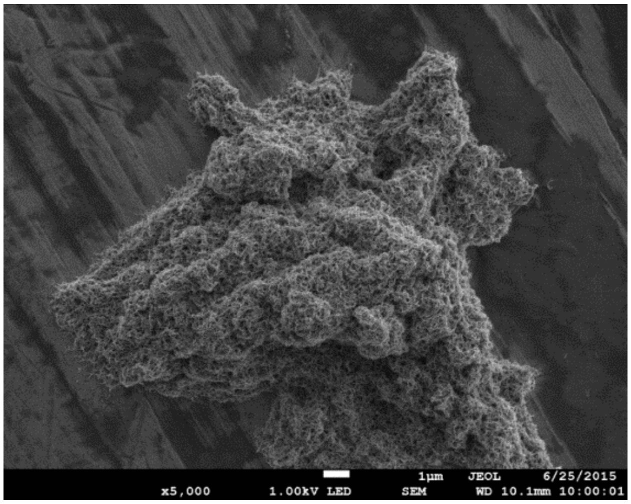
2. This is an action for infringement of U.S. Patent Nos. 8,475,961 ("the '961 Patent"), 9,636,649 ("the '649 Patent"), and 10,608,282 ("the '282 Patent") (collectively "the Asserted Patents") under the patent laws of the United States, 35 U.S.C. §§ 1, *et seq.*

3. Molecular Rebar Design, LLC ("MRD"), formed in 2012 and based in Austin, Texas, along with its affiliated predecessors going back to in or around 2009, recognized that there was a significant gap between the theoretical performance of carbon nanotubes (CNTs) and their

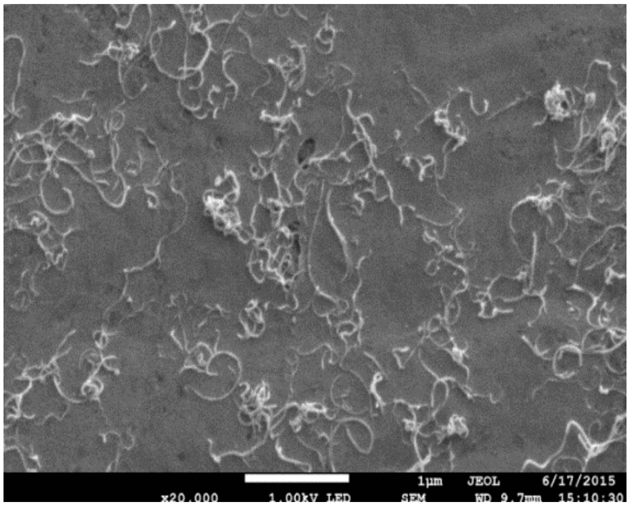
commercial viability because of their poor dispersibility. MRD has bridged that gap with unique capabilities to provide discrete, and optionally surface tailored carbon nanotubes.

4. MRD, with its extensive laboratory capabilities and multi-disciplinary nanotechnology expertise, has developed and commercialized a breakthrough form of modified CNTs called MOLECULAR REBAR® materials. These are the world's first CNTs that were substantially disentangled from the usual clumping and individualized through patent-protected processes which enable significantly enhanced performance for a myriad of high-value materials. MRD's cutting-edge technologies are protected by over 35 U.S. patents and over 80 foreign patents.

5. Example of bundled, non-discrete, multi-walled carbon nanotubes:



6. Example of disaggregated, de-bundled, discrete, exfoliated multi-walled carbon nanotubes:



7. Black Diamond Structures, LLC ("BDS"), formed in 2014, is a global nanotechnology leader partnering with manufacturers to create next generation world-class batteries. BDS's products are based on MRD's proprietary MOLECULAR REBAR® technology.

8. MRD is owner of the Asserted Patents, and BDS has an exclusive license to the Asserted Patents from MRD. MRD and BDS together possess all rights in the Asserted Patents to bring this lawsuit and seek all relief and damages for the patent infringement alleged herein.

THE PARTIES

9. MRD is a Delaware limited liability company with a principal place of business at 13477 Fitzhugh Rd, Austin, TX 78736.

10. BDS is a Delaware limited liability company with a principal place of business at 12310 Trail Driver, Austin, TX 78737.

11. On information and belief, Defendant LG Chem, Ltd. is a South Korean corporation with its principal place of business at 128 Yeoui-daero, Yeongdeungpo-gu, Seoul 7336, South Korea.

12. On information and belief, Defendant LG Energy Solution, Ltd. ("LGES") is a corporation organized under the laws of South Korea, having a principal place of business at 108 Yeouidaero, Yeongdeungpo-gu, Seoul 07335, South Korea.

13. On information and belief, Defendant LG Energy Solution Michigan, Inc. ("LGESM") is a corporation organized and existing under the laws of the State of Delaware and maintains its principal place of business at 1 LG Way, Holland, Michigan 49423.

14. On information and belief, LGESM is a wholly owned subsidiary of LGES and was formerly named LG Chem Michigan, Inc., until its name was changed to LG Energy Solution Michigan, Inc. on or about December 1, 2020.

15. On information and belief, LGESM may be served with process through its registered agent Corporation Service Company at 251 Little Falls Drive, Wilmington, Delaware 19808.

16. Defendants LG Chem, Ltd., LG Energy Solution, Ltd., and LG Energy Solution Michigan, Inc. are referred to collectively as "LG Chem."

17. On information and belief, Defendant LG Electronics, Inc. ("LGE") is a South Korean corporation with a principal place of business at LG Twin Towers, 128 Yeoui-daero, Yeongdungpo-gu, Seoul, 07366, South Korea.

JURISDICTION AND VENUE

18. This Court has exclusive subject matter jurisdiction over this case under 28 U.S.C. §§ 1331 and 1338.

19. Venue is proper in this Court under 28 U.S.C. §§ 1391 and 1400(b). LG Chem, Ltd., LG Energy Solution, Ltd., and LG Electronics, Inc. are foreign entities, and thus, venue is proper in this judicial district. On information and belief, all of the Defendants have committed

acts of infringement in this judicial district and have purposefully transacted business involving the accused products in the United States and this judicial district.

20. This Court has personal jurisdiction over the Defendants because: (1) Plaintiffs' claims arise in whole or in part from Defendants' conduct in the State of Delaware; (2) LG Chem, Ltd. has sought the protection and benefit from the laws of the State of Delaware and regularly conducts business in the State of Delaware by incorporating subsidiaries, including LG Energy Solution Michigan, Inc., in the State of Delaware; (3) all of the Defendants regularly conduct business throughout the United States, including the State of Delaware, and contract to supply services or things in Delaware; (4) all of the Defendants have contacts purposefully directed at the United States and the State of Delaware and have continuous and systematic contacts with the United States and the State of Delaware; (5) all of the Defendants have placed infringing products into the stream of commerce through an established distribution channel with the expectation or knowledge that they will be purchased by consumers in the United States and the State of Delaware; and (6) all of the Defendants have caused tortious injury in the State of Delaware.

21. Defendant LG Chem, Ltd. maintains a United States version of its website at https://www.lgchem.com/us/main. On this website, LG Chem, Ltd. provides information regarding its activities and products, including LG Chem, Ltd.'s Lithium Batteries, which include the infringing batteries and systems. On information and belief, LG Chem, Ltd.'s website is directed to marketing, offering for sale, and sales of its products and services in the United States and in the State of Delaware.

22. Defendant LG Electronics, Inc. maintains a United States version of its website at https://www.lg.com/us. On this website, LG Electronics, Inc. provides information regarding its activities and products. On information and belief, LG Electronics, Inc.'s website is directed to

marketing, offering for sale, and sales of its products and services in the United States and in the State of Delaware.

23. Defendant LG Energy Solution, Ltd. maintains an English version of its website at https://www.lgensol.com/en. On this website, LGES provides information regarding its activities and products, including information relating to its manufacturing facility in Holland, Michigan. On information and belief, LGES's website is directed to marketing, offering for sale, and sales of its products and services in the United States and in the State of Delaware.

24. Defendants LG Chem, Ltd., LG Energy Solution, Ltd., and LG Electronics, Inc. have also derived benefits from the laws of the United States. For example, Defendants LG Chem, Ltd., LG Energy Solution, Ltd., and LG Electronics, Inc. have filed litigations in the United States, including based on claims for patent infringement. On information and belief, Defendants LG Chem, Ltd., LG Energy Solution, Ltd., and LG Electronics, Inc. derive substantial revenues from their regularly conducted business activities throughout the United States and the State of Delaware. On information and belief, Defendants LG Chem, Ltd., LG Energy Solution, Ltd., and LG Electronics, Inc. receive substantial revenue from their activities and the activities of their U.S. subsidiaries in the United States. On information and belief, Defendants LG Chem, Ltd., LG Energy Solution, Ltd., and LG Electronics, Inc. are in regular contact with their subsidiaries and affiliates in the United States and direct communication into the United States.

THE ASSERTED PATENTS

25. On July 2, 2013, the United States Patent and Trademark Office duly and legally issued the '961 Patent, titled "HIGH PERFORMANCE ENERGY STORAGE AND COLLECTION DEVICES CONTAINING EXFOLIATED MICROTUBULES AND SPATIALLY CONTROLLED ATTACHED NANOSCALE PARTICLES AND LAYERS." The '961 Patent has a filing date of December 14, 2010 and claims benefit to a provisional filing date

filed on December 18, 2009. Plaintiffs own all rights to the ’961 Patent necessary to bring this action, including the exclusive right to recover for past infringement. A true and correct copy of the ’961 Patent is attached as Exhibit 1 hereto.

26. The ’961 Patent describes energy storage or collection devices and methods for making such devices having electrode materials containing exfoliated carbon nanotubes with attached electro- or photoactive nanoscale particles or layers. The exfoliated carbon nanotubes and attached nanoscale particles or layers may be fabricated by methods such as coating, solution or casting or melt extrusion to form electrodes. Electrolytes may also be used for dispersing nanotubes and also in a polymeric form to allow melt fabrication methods.

27. On May 2, 2017, the United States Patent and Trademark Office duly and legally issued the ’649 Patent, titled “DISPERSIONS COMPRISING DISCRETE CARBON NANOTUBE FIBERS.” The ’649 Patent has a filing date of October 7, 2016 and a priority filing date of December 14, 2010. Plaintiffs own all rights to the ’649 Patent necessary to bring this action, including the exclusive right to recover for past infringement. A true and correct copy of the ’649 Patent is attached as Exhibit 2 hereto.

28. The ’649 Patent describes carbon nanotubes as composites with materials such as elastomers, thermosets and thermoplastics or aqueous dispersions of open-ended carbon nanotubes with additives. A further feature of this invention relates to the development of a concentrate of carbon nanotubes with an elastomer wherein the concentrate can be further diluted with an elastomer and other polymers and fillers using conventional melt mixing equipment.

29. On March 31, 2020, the United States Patent and Trademark Office duly and legally issued the ’282 Patent, titled “BINDERS, ELECTROLYTES AND SEPARATOR FILMS FOR ENERGY STORAGE AND COLLECTION DEVICES USING DISCRETE CARBON

NANOTUBES." The '282 Patent has a filing date of January 26, 2018 and an effective filing date of June 21, 2012. Plaintiffs own all rights to the '282 Patent necessary to bring this action, including the exclusive right to recover for past infringement. A true and correct copy of the '282 Patent is attached as Exhibit 3 hereto.

30. The '282 Patent describes in various embodiments an improved binder composition, electrolyte composition and a separator film composition using discrete carbon nanotubes. Their methods of production and utility for energy storage and collection devices, like batteries, capacitors and photovoltaics, is described. The binder, electrolyte, or separator composition can further comprise polymers. The discrete carbon nanotubes further comprise at least a portion of the tubes being open ended and/or functionalized. The utility of the binder, electrolyte or separator film composition includes improved capacity, power or durability in energy storage and collection devices. The utility of the electrolyte and or separator film compositions includes improved ion transport in energy storage and collection devices.

GENERAL ALLEGATIONS

31. Plaintiffs incorporate by reference the preceding paragraphs.

32. The products that infringe one or more claims of the Asserted Patents include but are not limited to Defendants' HG2, HG6, and MJ1 batteries ("Accused Products"). *See, e.g.*, Exhibit 4 attached hereto (HG2 datasheet); Exhibit 5 attached hereto (HG6 datasheet); Exhibit 6 attached hereto (MJ1 datasheet).

33. On information and belief, LG Chem has and continues to directly infringe one or more claims of each of the Asserted Patents in violation of 35 U.S.C. § 271(a).

34. On information and belief, LG Chem has and continues to indirectly infringe and/or contribute to the infringement of one or more claims of each of the Asserted Patents in violation of 35 U.S.C. § 271 (b) and (c) at least based on its activities in Michigan.

35. On information and belief, LGE has and continues to directly and indirectly infringe one or more claims of each of the Asserted Patents in violation of 35 U.S.C. §§ 271(a), (b), and (c).

36. Defendants are knowledgeable about the Asserted Patents and their infringing acts at least as of the date on which they are properly served with this Complaint.

37. Defendants' acts of infringement have caused damage to Plaintiffs. Plaintiffs are entitled to recover from Defendants the past damages sustained by Plaintiffs as a result of Defendants' wrongful acts in an amount to be proven at trial. In the event Defendants are not enjoined from future infringing activity, Plaintiffs are also entitled to recover from Defendants a compulsory future royalty payable on each infringing product made, used, or sold by Defendants following trial or that is not captured in the damages awarded to Plaintiffs.

CLAIMS FOR PATENT INFRINGEMENT

38. Plaintiffs incorporate by reference the preceding paragraphs.

39. Plaintiffs identify below exemplary claims of the Asserted Patents to demonstrate infringement by exemplary products. However, the selection of exemplary claims and exemplary products should not be considered limiting, and additional infringing products and infringed claims of the Asserted Patents will be disclosed in compliance with the Court's rules related to infringement contentions as discovery progresses.

COUNT I: INFRINGEMENT OF THE '961 PATENT

40. Plaintiffs incorporate by reference the preceding paragraphs.

41. On information and belief, LGE directly infringes, induces the infringement of, and contributes to the infringement of one or more claims of the '961 Patent, including at least claim 1, either literally or under the doctrine of equivalents.

42. On information and belief, LGE directly infringes the ’961 Patent by, for example, assembling, or causing to have assembled, one or more of the Accused Products for use in third party electric vehicles.

43. On information and belief, LGE induces the infringement of the ’961 Patent by third parties, including without limitation automobile manufactures or other device makers, by actively encouraging third parties to make, use, offer to sell, sell, or import into the United States, for example, electric vehicles or other consumer electronics containing the infringing battery technologies. For example, LGE instructs, offers, or encourages third party automobile manufacturers to use one or more of the Accused Products in electric vehicles.

44. On information and belief, LGE contributes to the infringement of the ’961 Patent by offering to sell or selling within the United States or importing into the United States infringing battery technologies for use in at least electric vehicles or other consumer electronics sold in the United States, knowing the infringing battery technologies to be especially-made components that have no substantial non-infringing use.

45. On information and belief, LG Chem at least induces the infringement of one or more claims of the ’961 Patent, including at least claim 1, either literally or under the doctrine of equivalents.

46. On information and belief, LG Chem induces LGE to infringe the ’961 Patent by instructing, offering, and encouraging LGE to use LG Chem’s infringing battery technologies in LGE products.

47. On information and belief, LG Chem designs battery cells for the United States EV market and competes for business that it knows is directed to downstream products designated for the United States market. For example, LGES maintains a website specifically tailored for the

United States and notes that it supplies automotive batteries for automobiles that are sold and offered for sale in the United States. *See* https://www.lgensol.com/en/business-automotive-battery (last accessed August 10, 2022).

48. On information and belief, LG Chem has directly infringed and/or contributed to the infringement of, and will continue to infringe and/or contribute to the infringement of, one or more claims of the '961 Patent at least based on its activities in Michigan. *See, e.g.*, *LG Chem, Ltd. v. SK Innovation Co., Ltd.*, 1:19-cv-00776 (D. Del. April 29, 2019), Complaint, ¶ 29 ("LGCMI also has research and development, testing and engineering, manufacturing, sales and marketing, and business offices in Troy, Michigan, where it has invested many millions of dollars and employs hundreds of workers. Through its facilities in Michigan, LGC supplies millions of battery cells each year to automotive manufacturers including General Motors and Chrysler."); *LG Energy Solution, Ltd. et al. v. SK Innovation Co., Ltd. et al.*, 19-cv-1805-CFC, D.I. 12-1 (D. Del. Jan. 5, 2021) ("LGES has extensive involvement in the U.S. market with its innovative battery technology. In fact, LGES and its subsidiary LG Energy Solution Michigan [,] Inc. [ ] supply, through plants in Michigan[,] millions of battery cells to U.S. companies like General Motors and Chrysler. For example, LGESMI has invested hundreds of millions of dollars in a facility in Holland, Michigan, which employs hundreds of workers making lithium-ion batteries for electric vehicles (EVs).").

49. Further, on information and belief, LG Chem contributes to the infringement of the '961 Patent by offering to sell or selling within the United States or importing into the United States infringing battery technologies for use in at least electric vehicles or other consumer electronics sold in the United States, knowing the infringing battery technologies to be especially-made components that have no substantial non-infringing use. *See, e.g.*,

https://www.lgchem.com/company/company-information/global-network/overseas-corporation/america (last accessed August 29, 2022).

50. Defendants are knowledgeable about the ’961 Patent and infringing acts alleged herein at least as of the date on which they are served with this Complaint.

51. Defendants’ infringing acts have been without the permission, consent, authorization, or license of Plaintiffs.

52. Claim 1 of the ’961 Patent recites as follows:

1. An energy storage and collection device comprising:

a) at least two electrodes;

b) at least one of the electrodes containing carbon or mineral nanotubes that have been exfoliated from their as-synthesized state and have attached electroactive or photo active nanoscale particles or layers;

c) at least two current collectors, each in contact with an electrode, or the electrode also functions as the current collector; and

d) optionally an insulator.

53. Defendants, by the Accused Products, infringe at least claim 1 of the ’961 Patent.

54. Each of the Accused Products is an energy storage and collection device.

LG HG2

LG HG6

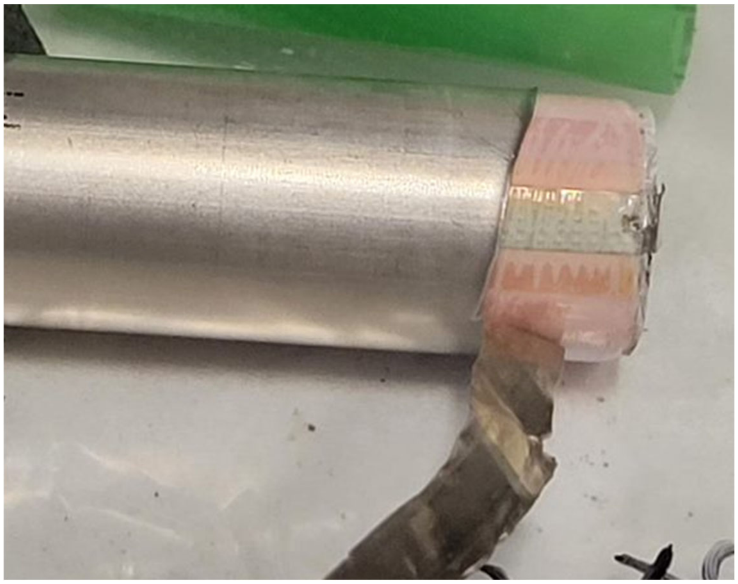
LG MJ1

55. The Accused Products have at least two electrodes, namely, for example, cathode active materials laminated on to aluminum current collectors and anode active materials laminated on to copper current collectors, with tabs protruding from opposite ends of the cylinder.

LG HG2

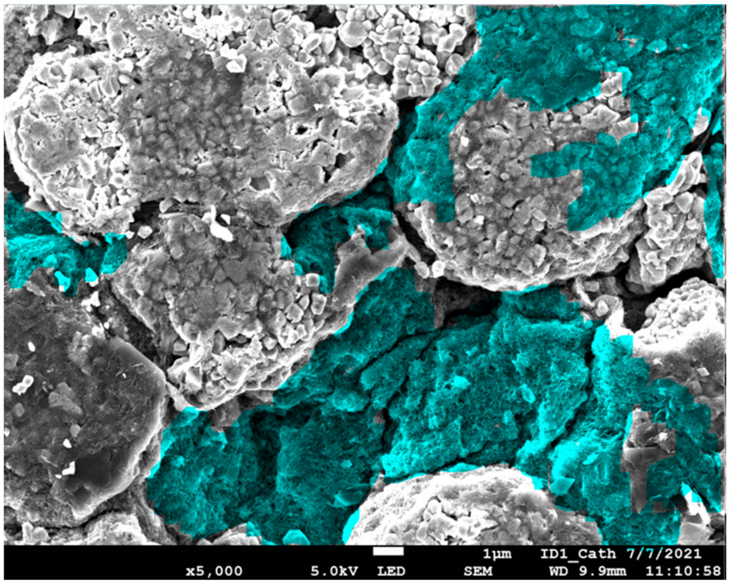
LG HG6

LG MJ1

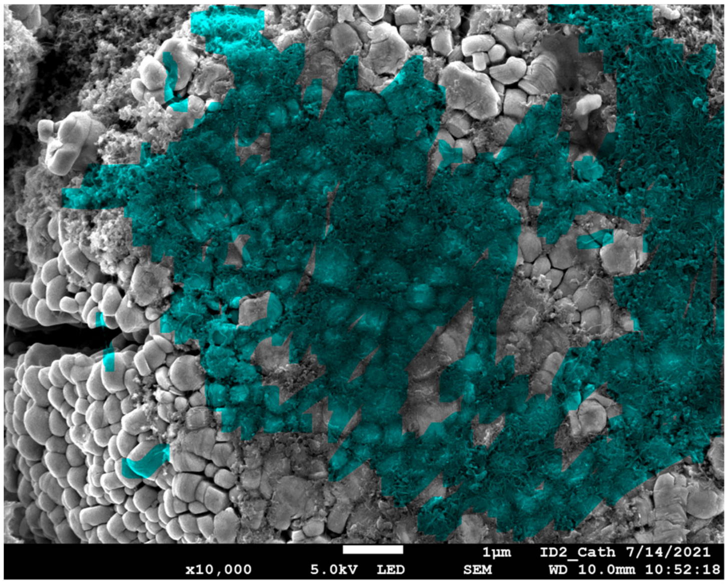


56. At least one of the electrodes of each of the Accused Products contain carbon or mineral nanotubes (reflected by the blue highlighted regions in the below scanning electron microscope (SEM) images).

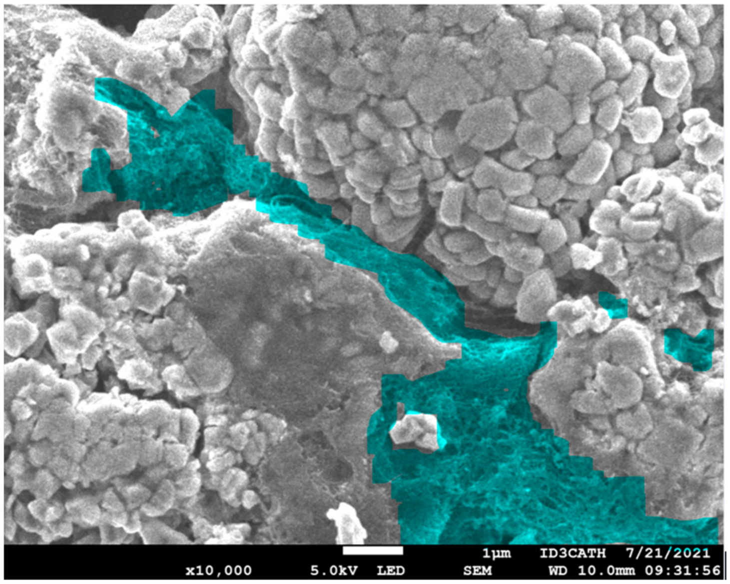
LG HG2


1µm
ID1_Cath 7/7/2021
x5,000
5.0kV
LED
SEM
WD 9.9mm
11:10:58

LG HG6

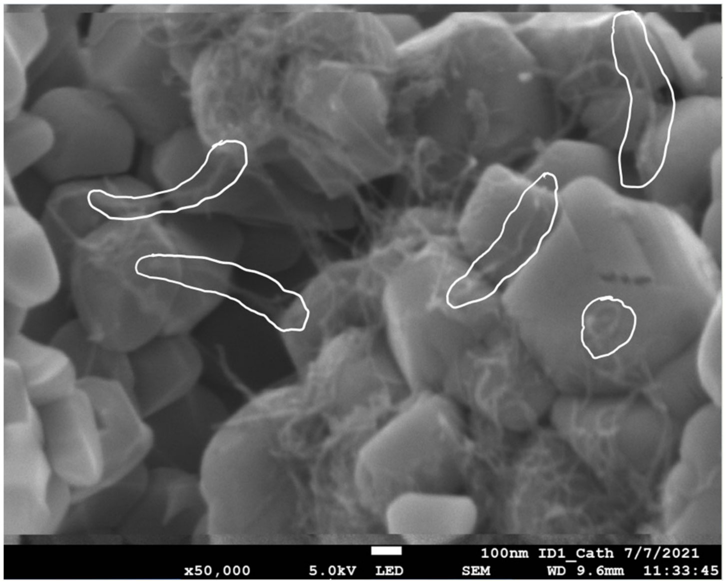

1µm
ID2_Cath 7/14/2021
x10,000
5.0kV
LED
SEM
WD 10.0mm
10:52:18

LG MJ1

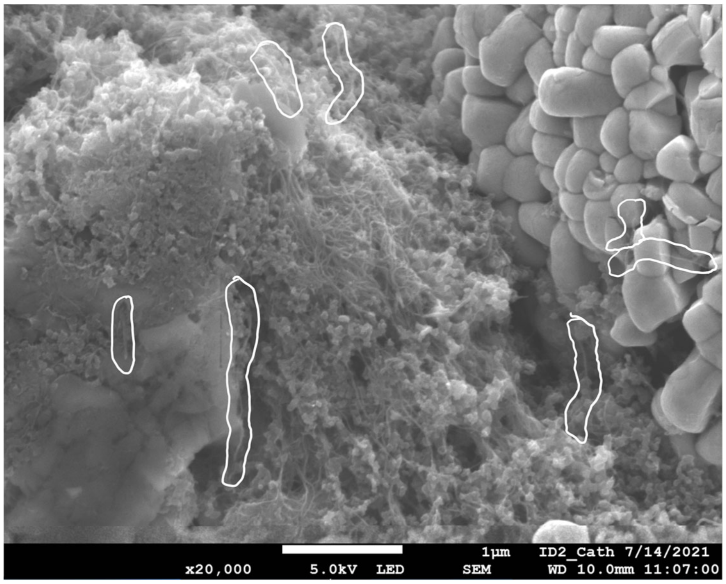


57. The aforementioned CNTs of the Accused Products have been exfoliated (de-aggregated, separated, individualized) as shown by the white circled regions in the below SEM images.

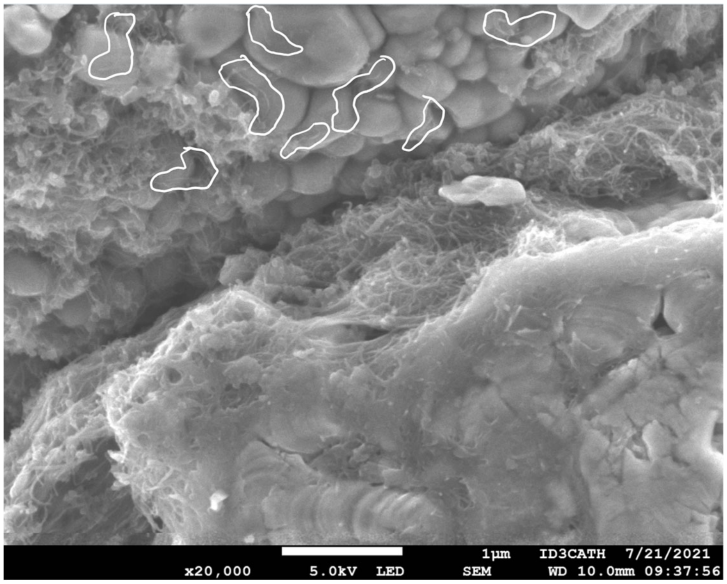
LG HG2



LG HG6

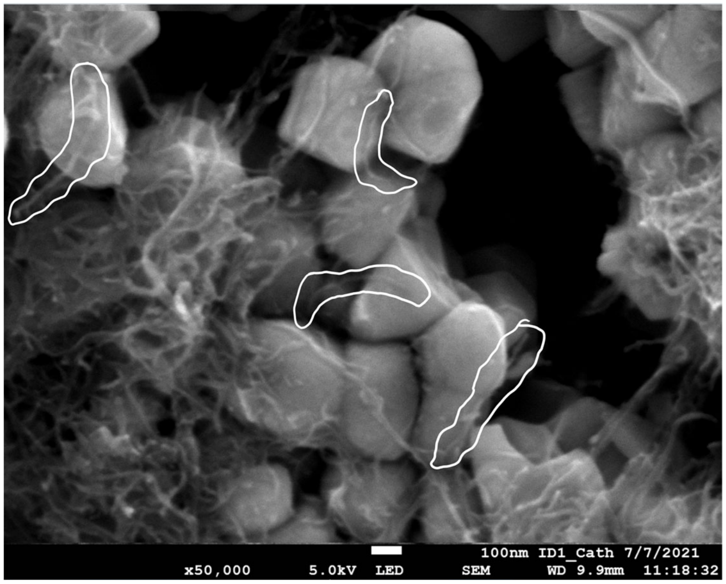


LG MJ1

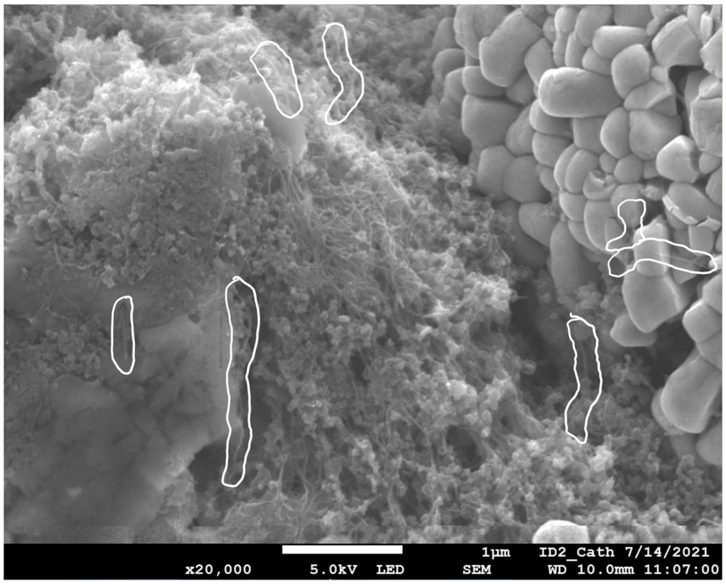


58. The aforementioned CNTs have attached electroactive or photo active nanoscale particles or layers as shown by the white circled regions in the below SEM images.

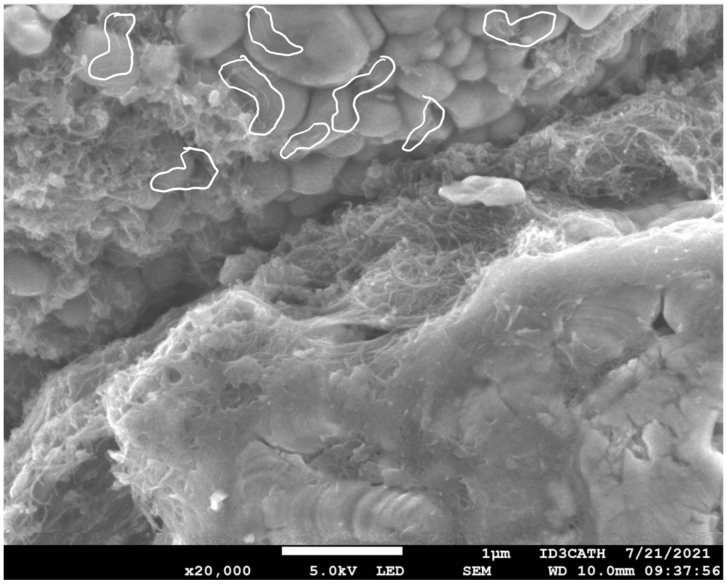
LG HG2


100nm ID1_Cath 7/7/2021
x50,000 5.0kV LED SEM WD 9.9mm 11:18:32

LG HG6


1μm ID2_Cath 7/14/2021
x20,000 5.0kV LED SEM WD 10.0mm 11:07:00

LG MJ1

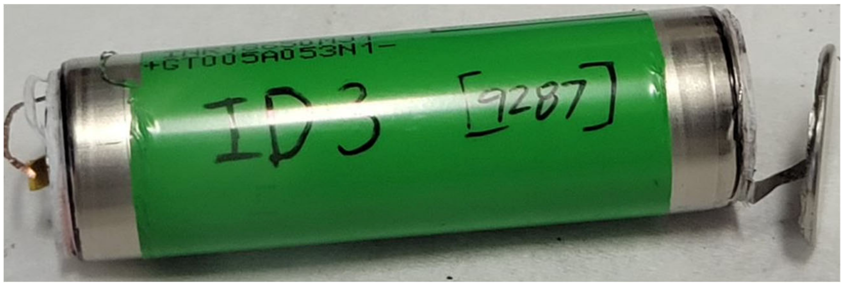


59. The Accused Products have at least two current collectors – *e.g.*, the anode (copper, orange/shiny) and the cathode (aluminum, silver/shiny).

LG HG2

LG HG6

LG MJ1



60. The Accused Products use electrodes laminated (deposited as a liquid slurry and dried) to the current collector (anode – copper, cathode – aluminum).

61. The Accused Products have an insulator functioning to physically distance the anode and cathode electrodes (white wrapping in images above).

COUNT II: INFRINGEMENT OF THE ’649 PATENT

62. Plaintiffs incorporate by reference the preceding paragraphs.

63. On information and belief, LGE directly infringes, induces the infringement of, and contributes to the infringement of one or more claims of the ’649 Patent, including at least claim 1, either literally or under the doctrine of equivalents.

64. On information and belief, LGE directly infringes the ’649 Patent by, for example, assembling, or causing to have assembled, one or more of the Accused Products for use in third party electric vehicles.

65. On information and belief, LGE induces the infringement of the ’649 Patent by third parties, including without limitation automobile manufactures, by actively encouraging third parties to make, use, offer to sell, sell, or import into the United States, electric vehicles containing the infringing battery technologies. For example, LGE instructs, offers, or encourages third party automobile manufacturers to use one or more of the Accused Products in electric vehicles.

66. On information and belief, LGE contributes to the infringement of the ’649 Patent by offering to sell or selling within the United States or importing into the United States infringing battery technologies for use in at least electric vehicles sold in the United States, knowing the infringing battery technologies to be especially-made components that have no substantial non-infringing use.

67. On information and belief, LG Chem at least induces the infringement of one or more claims of the ’649 Patent, including at least claim 1, either literally or under the doctrine of equivalents.

68. On information and belief, LG Chem induces LGE to infringe the ’649 Patent by instructing, offering, and encouraging LGE to use LG Chem’s infringing battery technologies in LGE products.

69. On information and belief, LG Chem designs battery cells for the United States EV market and competes for business that it knows is directed to downstream products designated for the United States market. For example, LGES maintains a website specifically tailored for the United States and notes that it supplies automotive batteries for automobiles that are sold and offered for sale in the United States. *See* https://www.lgensol.com/en/business-automotive-battery (last accessed August 10, 2022).

70. On information and belief, LG Chem has directly infringed and/or contributed to the infringement of, and will continue to infringe and/or contribute to the infringement of, one or more claims of the ’649 Patent at least based on its activities in Michigan. *See, e.g.*, *LG Chem, Ltd. v. SK Innovation Co., Ltd.*, 1:19-cv-00776 (D. Del. April 29, 2019), Complaint, ¶ 29 (“LGCMI also has research and development, testing and engineering, manufacturing, sales and marketing, and business offices in Troy, Michigan, where it has invested many millions of dollars and employs hundreds of workers. Through its facilities in Michigan, LGC supplies millions of battery cells each year to automotive manufacturers including General Motors and Chrysler.”); *LG Energy Solution, Ltd. et al. v. SK Innovation Co., Ltd. et al.*, 19-cv-1805-CFC, D.I. 12-1 (D. Del. Jan. 5, 2021) (“LGES has extensive involvement in the U.S. market with its innovative battery technology. In fact, LGES and its subsidiary LG Energy Solution Michigan [,] Inc. [ ] supply, through plants in Michigan[,] millions of battery cells to U.S. companies like General Motors and Chrysler. For example, LGESMI has invested hundreds of millions of dollars in a facility in Holland, Michigan, which employs hundreds of workers making lithium-ion batteries for electric vehicles (EVs).”).

71. Further, on information and belief, LG Chem contributes to the infringement of the ’961 Patent by offering to sell or selling within the United States or importing into the United States infringing battery technologies for use in at least electric vehicles or other consumer electronics sold in the United States, knowing the infringing battery technologies to be especially-made components that have no substantial non-infringing use. *See, e.g.*, https://www.lgchem.com/company/company-information/global-network/overseas-corporation/america (last accessed August 29, 2022).

72. Defendants are knowledgeable about the ’649 Patent and infringing acts alleged herein at least as of the date on which they are served with this Complaint.

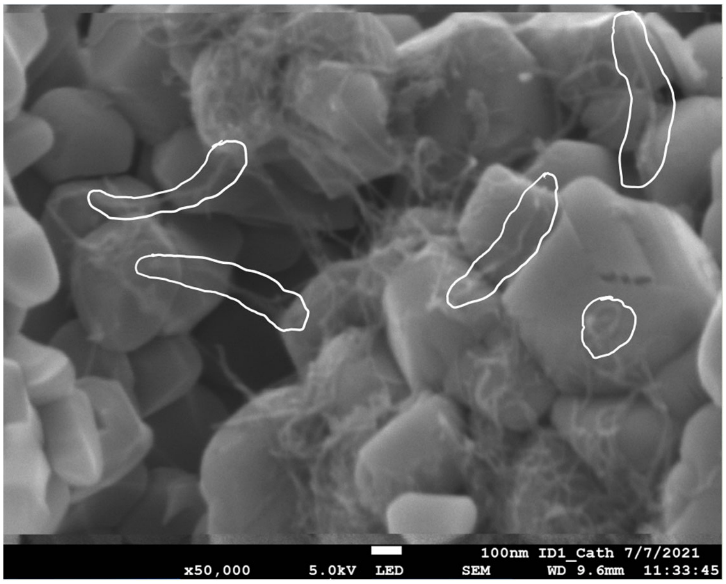
73. Defendants’ infringing acts have been without the permission, consent, authorization, or license of Plaintiffs.

74. Claim 1 of the ’649 Patent recites as follows:

> 1. A dispersion comprising a plurality of oxidized, discrete carbon nanotubes and at least one additive, wherein the oxidized, discrete carbon nanotubes have an aspect ratio of 25 to 500, are multiwall, and are present in the range of greater than zero to about 30% by weight based on the total weight of the dispersion.

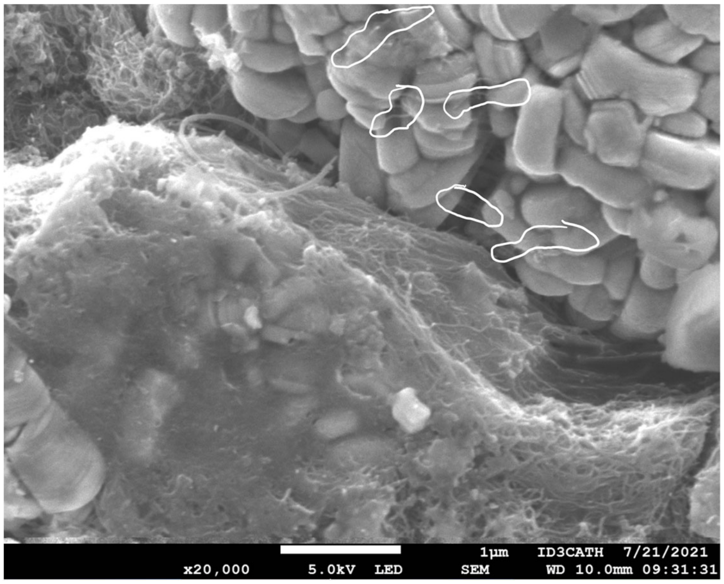
75. Defendants, by the Accused Products, infringe at least claim 1 of the ’649 Patent.

76. The Accused Products contain a plurality of oxidized, discrete carbon nanotubes as reflected by the white circled regions in the below SEM image.



77. Each of the Accused Products have cathodes with an added component (“additive”) that is in composition with the nanotubes, where the oxidized, discrete carbon nanotubes have an

aspect ratio of 25 to 500 and are multiwall, as shown by the white circled regions in the below SEM image.



78. The nanotubes present in the Accused Products are present in the range of greater than zero to about 30% by weight based on the total weight of the dispersion. On information and belief, the nanotubes in the Accused Products are present in an amount of less than about 10% of the cathode.

COUNT III: INFRINGEMENT OF THE ’282 PATENT

79. Plaintiffs incorporate by reference the preceding paragraphs.

80. On information and belief, LGE directly infringes, induces the infringement of, and contributes to the infringement of one or more claims of the ’282 Patent, including at least claim 1, either literally or under the doctrine of equivalents.

81. On information and belief, LGE directly infringes the ’282 Patent by, for example, assembling, or causing to have assembled, one or more of the Accused Products for use in third party electric vehicles.

82. On information and belief, LGE induces the infringement of the ’282 Patent by third parties, including without limitation automobile or consumer electronics manufactures, by actively encouraging third parties to make, use, offer to sell, sell, or import into the United States, electric vehicles containing the infringing battery technologies. For example, LGE instructs, offers, or encourages third party automobile manufacturers to use one or more of the Accused Products in electric vehicles.

83. On information and belief, LGE contributes to the infringement of the ’282 Patent by offering to sell or selling within the United States or importing into the United States infringing battery technologies for use in at least electric vehicles sold in the United States, knowing the infringing battery technologies to be especially-made components that have no substantial non-infringing use.

84. On information and belief, LG Chem at least induces the infringement of one or more claims of the ’282 Patent, including at least claim 1, either literally or under the doctrine of equivalents.

85. On information and belief, LG Chem induces LGE to infringe the ’282 Patent by instructing, offering, and encouraging LGE to use LG Chem’s infringing battery technologies in LGE products.

86. On information and belief, LG Chem designs battery cells for the United States EV market and competes for business that it knows is directed to downstream products designated for the United States market. For example, LGES maintains a website specifically tailored for the United States and notes that it supplies automotive batteries for automobiles that are sold and offered for sale in the United States. *See* https://www.lgensol.com/en/business-automotive-battery (last accessed August 10, 2022).

87. On information and belief, LG Chem has directly infringed and/or contributed to the infringement of, and will continue to infringe and/or contribute to the infringement of, one or more claims of the ’282 Patent at least based on its activities in Michigan. *See, e.g.*, *LG Chem, Ltd. v. SK Innovation Co., Ltd.*, 1:19-cv-00776 (D. Del. April 29, 2019), Complaint, ¶ 29 (“LGCMI also has research and development, testing and engineering, manufacturing, sales and marketing, and business offices in Troy, Michigan, where it has invested many millions of dollars and employs hundreds of workers. Through its facilities in Michigan, LGC supplies millions of battery cells each year to automotive manufacturers including General Motors and Chrysler.”); *LG Energy Solution, Ltd. et al. v. SK Innovation Co., Ltd. et al.*, 19-cv-1805-CFC, D.I. 12-1 (D. Del. Jan. 5, 2021) (“LGES has extensive involvement in the U.S. market with its innovative battery technology. In fact, LGES and its subsidiary LG Energy Solution Michigan [,] Inc. [ ] supply, through plants in Michigan[,] millions of battery cells to U.S. companies like General Motors and Chrysler. For example, LGESMI has invested hundreds of millions of dollars in a facility in Holland, Michigan, which employs hundreds of workers making lithium-ion batteries for electric vehicles (EVs).”).

88. Further, on information and belief, LG Chem contributes to the infringement of the ’961 Patent by offering to sell or selling within the United States or importing into the United States infringing battery technologies for use in at least electric vehicles or other consumer electronics sold in the United States, knowing the infringing battery technologies to be especially-made components that have no substantial non-infringing use. *See, e.g.*, https://www.lgchem.com/company/company-information/global-network/overseas-corporation/america (last accessed August 29, 2022).

89. Defendants are knowledgeable about the ’282 Patent and infringing acts alleged herein at least as of the date on which they are served with this Complaint.

90. Defendants’ infringing acts have been without the permission, consent, authorization, or license of Plaintiffs.

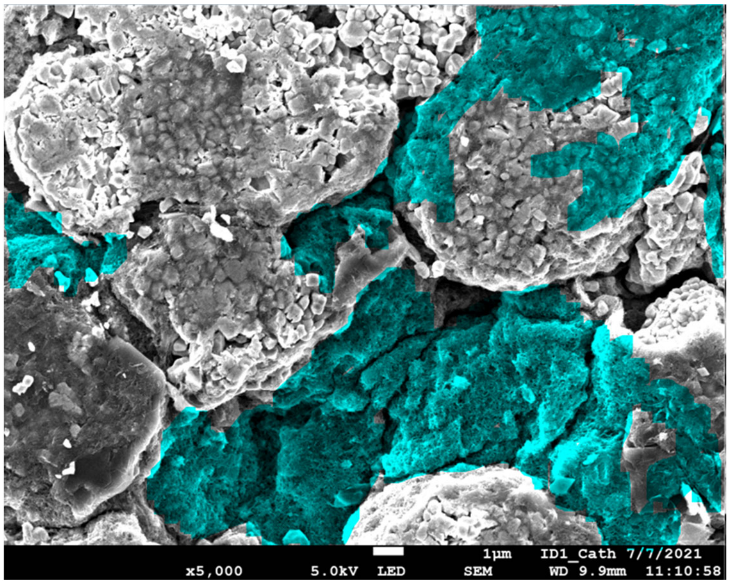
91. Claim 1 of the ’282 Patent recites as follows:

> 1. A composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising:
>
> a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended and
>
> wherein 40% to 90% by number of the discrete carbon nanotubes have an aspect ratio of 30-70 and wherein from 1% to 30% by number of discrete carbon nanotubes have an average aspect ratio 80-140.

92. Defendants, by the Accused Products, infringe at least claim 1 of the ’282 Patent.

93. The Accused Products have pluralities of carbon nanotube materials covering the surfaces of the active materials and binding the particles together in crevices as shown by the blue highlighting in the below SEM images. These nanotubes are being used as a binder, or part of a binder system.

LG HG2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x5,000
5.0kV
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SEM
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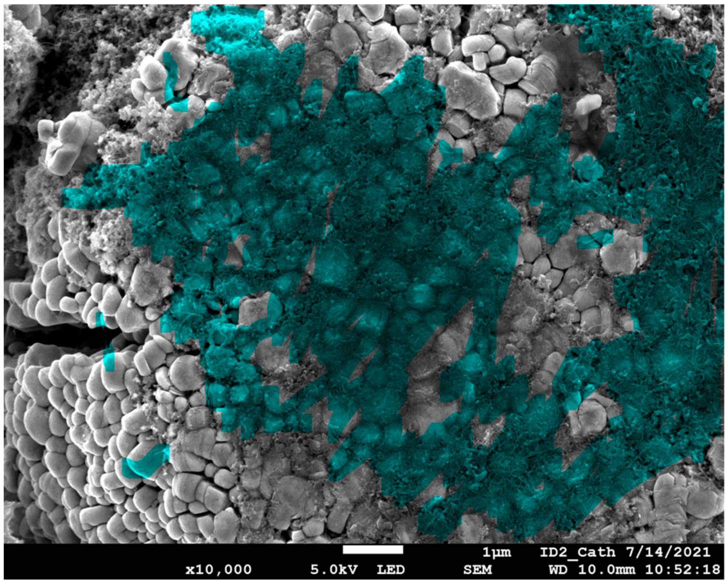
11:10:58

LG HG6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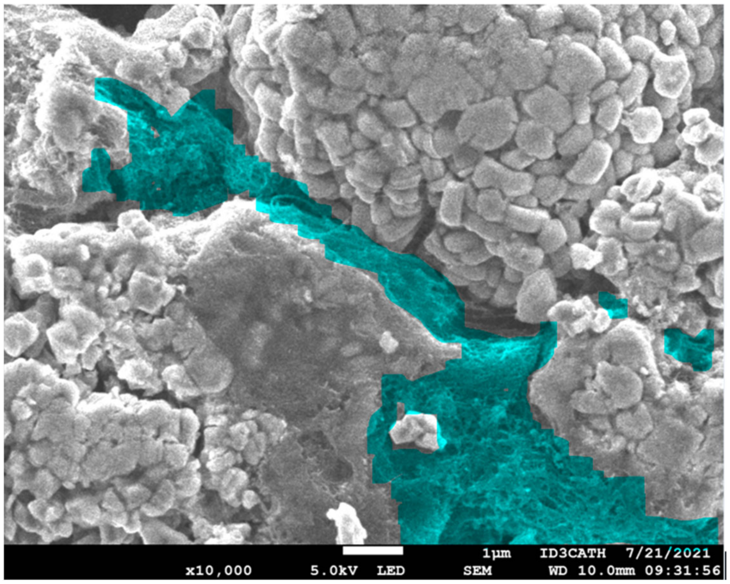
10:52:18

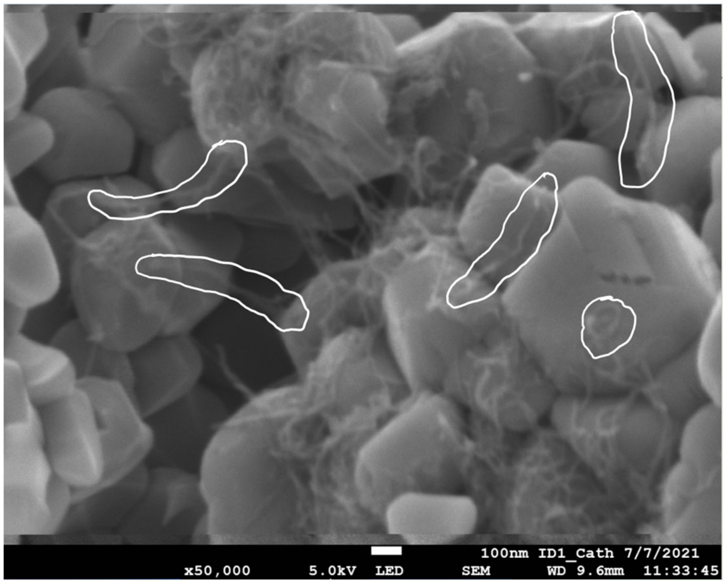
LG MJ1



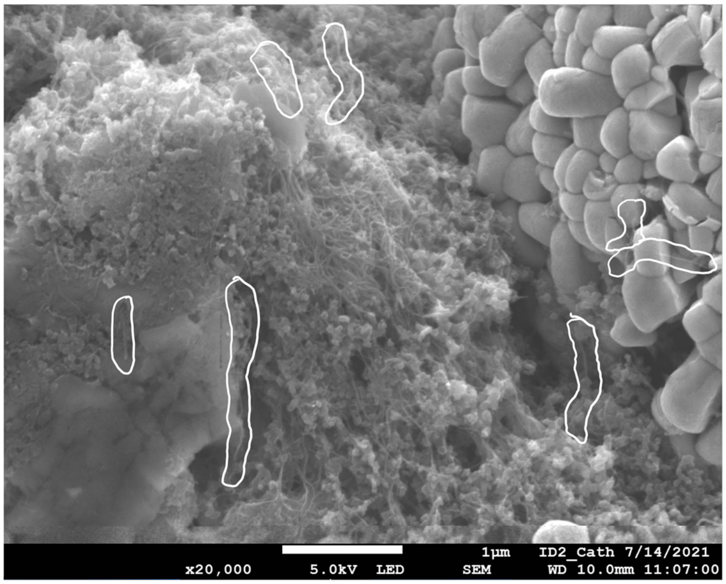
94. The aforementioned composition is of an energy storage or collection device, which the Accused Products are as previously set forth.

95. The Accused Products have a plurality of discrete carbon nanotube fibers as shown by the white circled regions in the below SEM images.

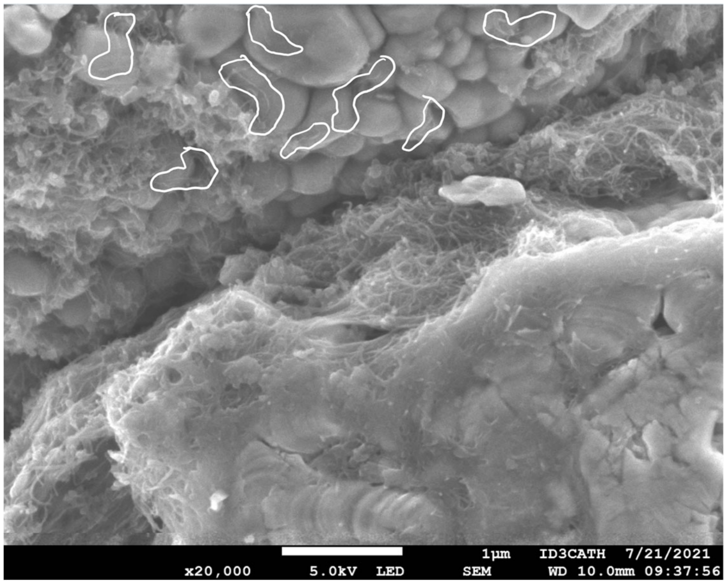
LG HG2



LG HG6



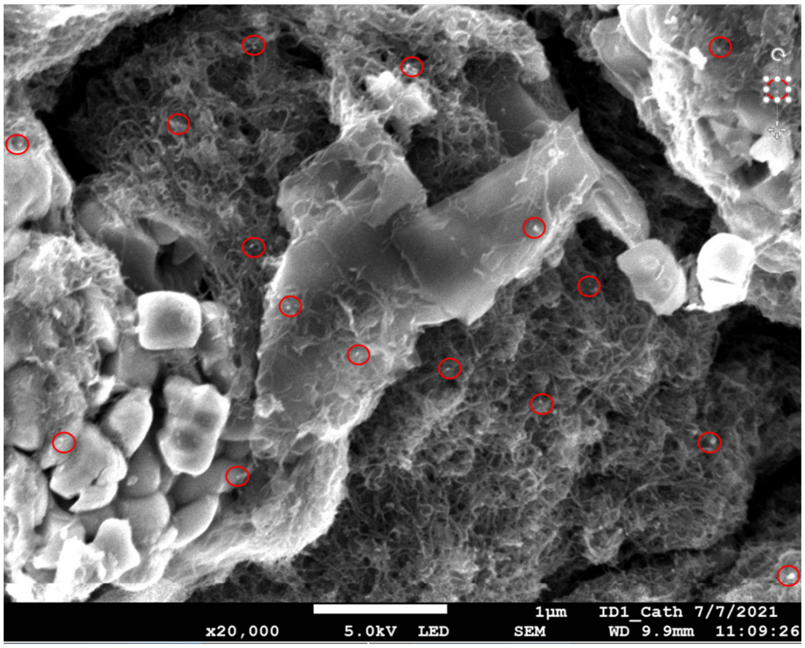
LG MJ1



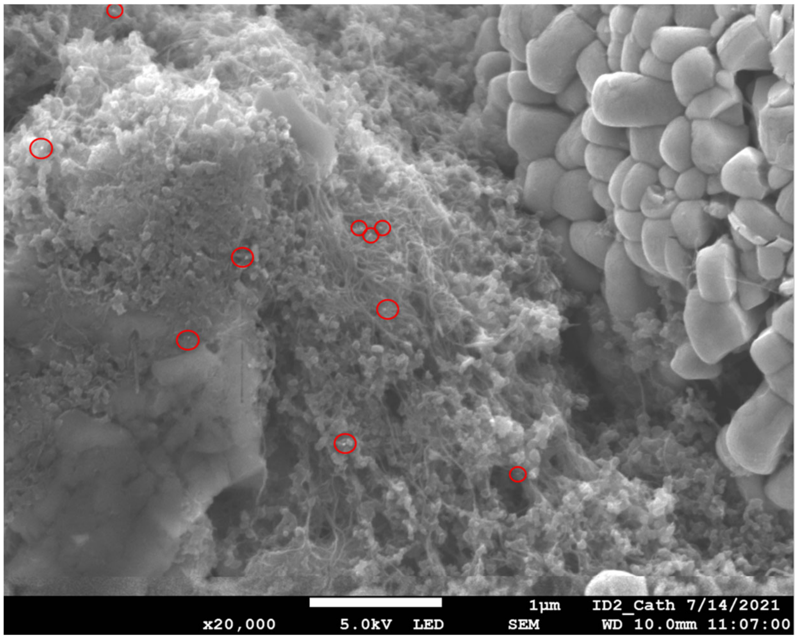
96. The aforementioned carbon nanotube fibers have an aspect ratio of from about 10 to about 500 based on SEM-based dimensional measurements showing nanotube lengths of approximately 500-2000 nm and diameters of approximately 10-20 nm, thus fitting within the claim range (aspect ratio = length divided by diameter).

97. A least a portion of the discrete carbon nanotube fibers in the Accused Products are open ended as shown by the red circled regions in the below SEM images.

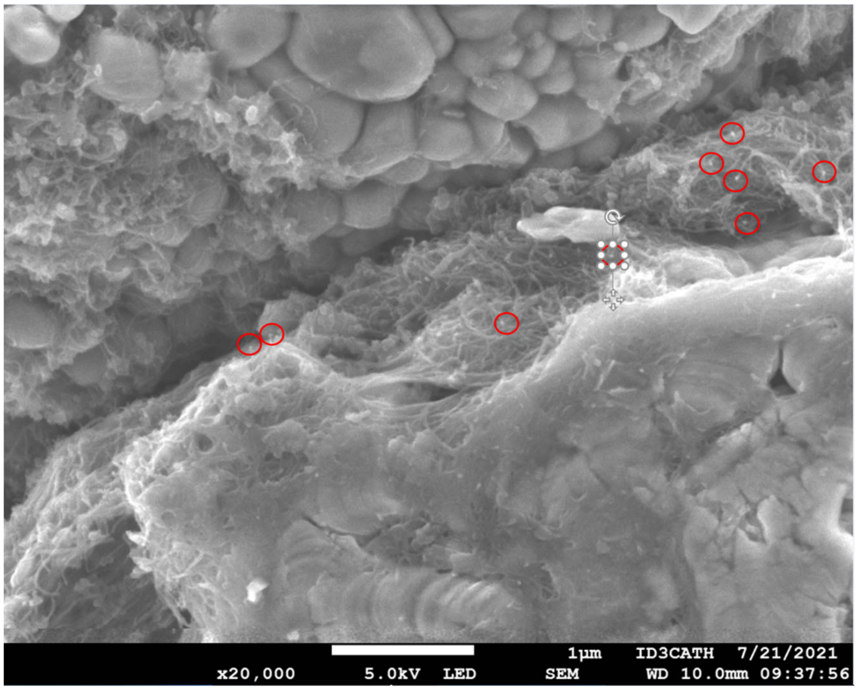
LG HG2



LG HG6



LG MJ1



98. In the Accused Products, 40% to 90% by number of the discrete carbon nanotubes have an aspect ratio of 30-70 based on SEM-based dimensional measurements of the detangled carbon nanotubes.

99. In the Accused Products, 1% to 30% by number of discrete carbon nanotubes have an average aspect ratio 80-140 based on SEM-based dimensional measurements of the detangled carbon nanotubes.

PRAYER FOR RELIEF

100. Plaintiffs incorporate by reference the preceding paragraphs.

101. As a result of Defendants' unlawful activities, Plaintiffs have suffered and will continue to suffer irreparable harm for which there is no adequate remedy at law. Defendants' continued infringement of the Asserted Patents causes harm to Plaintiffs in the form of price erosion, loss of goodwill, damage to reputation, loss of business opportunities, inadequacy of

money damages, and direct and indirect competition. Monetary damages are insufficient to compensate Plaintiffs for these harms. Accordingly, Plaintiffs are entitled to preliminary and permanent injunctive relief.

102. Under the law, Plaintiffs are also entitled to compensation for Defendants' infringement described above. However, the full compensation owed to Plaintiffs cannot be ascertained except through discovery and special accounting. To the fullest extent permitted by law, Plaintiffs seek recovery of at least reasonable royalties. Plaintiffs further seek any other damages to which Plaintiffs are entitled under law or in equity.

103. Plaintiffs are entitled to recover reasonable attorneys' fees under applicable law, including 35 U.S.C. § 285 given the exceptional nature of this case.

104. WHEREFORE, Plaintiffs pray that the Court enter the following relief under any applicable law, rule, or inherent power of the Court:

a. judgment that Defendants infringe the Asserted Patents;
b. judgment that Defendants' infringement of the Asserted Patents has been willful;
c. order of an accounting of damages;
d. damages in an amount adequate to compensate Plaintiffs for Defendants' infringement of the Asserted Patents, but in no event less than a reasonable royalty under 35 U.S.C. § 284, including supplemental damages for any continuing post-verdict infringement up until entry of the final judgment;
e. enhanced damages under 35 U.S.C. § 284;
f. pre-judgment and post-judgment interest to Plaintiffs to the full extent allowed under the law;
g. Plaintiffs' costs;

h. If permanent injunctive relief is not granted, a compulsory future royalty payable on each infringing product made, used, or sold by Defendants following trial or that is not captured in the damages awarded to Plaintiffs;

i. order finding that this is an exceptional case and awarding Plaintiffs their reasonable attorneys' fees under 35 U.S.C. § 285;

j. entry of an order that preliminarily and permanently enjoins the Defendants and their officers, employees, agents, servants, attorneys, instrumentalities, and/or those in privity with them, from continuing to infringe the Asserted Patents and for all further and proper injunctive relief under 35 U.S.C. § 283; and

k. such other relief as the Court may deem appropriate and just under the circumstances.

DEMAND FOR A JURY TRIAL

In accordance with Federal Rule of Civil Procedure 38, Plaintiffs hereby respectfully demand a trial by jury of all issues and claims so triable.

Dated: August 29, 2022

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EXHIBIT 1

(12) **United States Patent**
Bosnyak et al.

(10) **Patent No.: US 8,475,961 B2**
(45) **Date of Patent: Jul. 2, 2013**

(54) **HIGH PERFORMANCE ENERGY STORAGE AND COLLECTION DEVICES CONTAINING EXFOLIATED MICROTUBULES AND SPATIALLY CONTROLLED ATTACHED NANOSCALE PARTICLES AND LAYERS**

(75) Inventors: **Clive P. Bosnyak**, Dripping Springs, TX (US); **Kurt W. Swogger**, Austin, TX (US)

(73) Assignee: **Molecular Rebar Design, LLC**, Austin, TX (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 205 days.

(21) Appl. No.: **12/968,151**

(22) Filed: **Dec. 14, 2010**

(65) **Prior Publication Data**

US 2011/0151321 A1 Jun. 23, 2011

Related U.S. Application Data

(60) Provisional application No. 61/288,025, filed on Dec. 18, 2009.

(51) **Int. Cl.**
H01M 4/13 (2010.01)

(52) **U.S. Cl.**
USPC **429/231.8**; 429/209; 429/218.1; 977/734; 977/742; 977/745; 977/748; 977/948

(58) **Field of Classification Search**
None
See application file for complete search history.

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Primary Examiner — Cynthia Walls
(74) *Attorney, Agent, or Firm* — Jackson Walker L.L.P.

(57) **ABSTRACT**

The present disclosure relates to energy storage or collection devices and methods for making such devices having electrode materials containing exfoliated nanotubes with attached electro- or photoactive nanoscale particles or layers.

The exfoliated nanotubes and attached nanoscale particles or layers may be easily fabricated by methods such as coating, solution or casting or melt extrusion to form electrodes. Electrolytes may also be used for dispersing nanotubes and also in a polymeric form to allow melt fabrication methods.

27 Claims, No Drawings

HIGH PERFORMANCE ENERGY STORAGE AND COLLECTION DEVICES CONTAINING EXFOLIATED MICROTUBULES AND SPATIALLY CONTROLLED ATTACHED NANOSCALE PARTICLES AND LAYERS

RELATED APPLICATION INFORMATION

This application claims priority to U.S. Provisional patent application Ser. No. 61/288,025 filed Dec. 18, 2009, the disclosure of which is incorporated herein in its entirety.

FIELD OF THE INVENTION

This disclosure relates generally to improved energy storage or collection devices and particularly to batteries, ultracapacitors and photovoltaics utilizing components containing microtubules that have been exfoliated and have attached nanoscale particles or layers.

BACKGROUND OF THE INVENTION

Carbon nanotubes (CNTs) are considered attractive materials for use in energy storage devices because of the individual nanotube properties of high strength and electrical conductivity. Carbon nanotubes have been recognized to be potentially useful in lithium ion batteries because of the lithium ion intercalation with the graphene layers, as described in U.S. Pat. No. 7,060,390. The challenge with current widespread use of carbon nanotubes, particularly with single walled and doubled walled carbon nanotubes is the absence of a robust, efficient and innocuous method to completely debundle nanotube aggregates into an individually dispersed state (i.e., exfoliated state). Thus, the previous use of carbon nanotubes in energy storage devices have been limited in performance by not being able to fully access the active surface area. Likewise the CNTs are difficult to obtain of high purity (>about 96 percent by weight) through removal of their catalytic residues and non-tubular carbon structures arising from their synthesis.

The obstacle to exfoliating CNTs arises because immediately following their synthesis the tubes readily assemble into parallel configurations leading to what is commonly referred to as bundles or ropes. As a consequence formidable van der Waals binding energies of about 20 kbT for every nanometer of tube overlap result, and hence, formation of aggregates that are very difficult to separate completely occurs. To overcome the van der Waals forces various approaches have been employed, such as tube chemical functionalization, surfactants and the like. These approaches have only been successful at producing exfoliated nanotubes of higher yields after severe degradation of the initial tube length. Carbon nanotubes of much reduced length suffer from poorer strength and conductance and thus limit their full performance in energy storage or collection devices.

Aligned carbon nanotubes still have considerable van der Waals associations which cause local clumping of the carbon nanotubes and hence reduced active surface area. Also, the challenge with aligned carbon nanotubes composites is that cracking in the tube direction can occur more easily than randomly oriented carbon nanotube composites. Additionally, the cost associated with specialty techniques for growing the carbon nanotubes in vertical arrays and their handling in making commercial electrodes is thought to be prohibitively high.

Lithium, Li, ion batteries are receiving considerable attention in applications, ranging from portable electronics to electric vehicles, due to their superior energy density over other rechargeable battery technologies. However, demands for lighter, thinner, and higher capacity lithium ion batteries has necessitated a concerted development of both improved electrodes and electrolytes to extend battery capacity, cycle life, and charge-discharge rates while maintaining the highest degree of safety available.

Li-ion batteries for vehicles typically require three times higher energy densities than available at present to meet the volume/weight requirements and to reduce the number of cells in the battery and system cost. Li batteries are not intrinsically tolerant to abusive conditions such as a short circuit (including an internal short circuit), overcharge, over-discharge, crush, or exposure to fire and/or other high temperature environments. The use of Li chemistry in these larger (energy) batteries increases the urgency to address these issues. The ability to attain a 15 year life, or 300,000 HEV cycles, or 5,000 EV cycles are unproven in conventional Li ion batteries and are anticipated to be difficult due to undesirable volume expansions/failure at electrodes and side-reactions of Li with the electrolyte at voltages greater than about four volts.

Batteries generally include a cathode, an anode and an electrolyte. Commercially, the most popular material for the anode of a Li-ion battery is graphite. The cathode is generally one of three materials: a layered oxide, such as lithium cobalt oxide, one based on a polyanion, such as lithium iron phosphate, or a spinel, such as lithium manganese oxide. The common lithium ion battery as commercialized by Sony uses an inorganic compound, $LiCoO_2$ as the cathode material and graphite at the anode. The $LiCoO_2$ has a rhombohedral structure where Li and Co cations fill alternating layers of edge-sharing octahedral sites in a close packed oxygen array. During charging, lithium is de-intercalated from the cathode layers, transported across the separator membrane in an electrolyte medium, and then intercalated into the carbon anode. In the discharge process, the lithium ions are de-intercalated from the anode and intercalated again to the empty octahedral site between layers in the cathode. Depending on the choice of material for the anode, cathode, and electrolyte the voltage, capacity, life, and safety of a lithium ion battery can change dramatically. A challenge for batteries in general is to manage the heat generated at the anode during discharge. The heat causes degradation of the electrolyte and hence reduced energy capacity over time.

The specific energy density (per weight or per volume) is related to both the working voltage and the reversible capacity. The working voltage depends on the potential of the redox process and the reversible capacity is restricted by the reversible amount of lithium intercalation. The available redox pair should locate in a higher and suitable potential range and the structure of material should be stable in wide composition range in order to obtain a high capacity.

The electrochemical lithium insertion/extraction reactions involve both lithium Ions diffusion in the lattice and charge transfer process on the particle surface. Thus, the electrode's conductivity includes lithium ion conductivity in active material bulk and electronic conductivity of electrode. Higher electronic conductivity is helpful to keep the inner resistance low and gives an excellent power density. Routes to overcome this deficiency include reduction of particle size and increase in electronic conductivity by coating of conducting agent such as carbon, as described in WO 2009/133807.

Silicon nanowires would appear to have high potential for future battery applications because of their inherent storage capacity of 4200 mAh g^{-1}. However, silicon expands over 300% upon Li^+ insertion, leading to severe problems of cracking on charge/discharge cycling. US 2008/0280207 describes an anode structure consisting of a silicon layer (not nanowires) around a parallel array of carbon nanotubes as being beneficial for improved capacity. The silicon layer is deposited by using chemical vapor deposition of SiH_4. The carbon nanotubes are also not exfoliated.

Conducting or high dielectric polymers such polyaniline, polypyrrole and polyvinylidene fluoride are often selected for binders of electro active particles.

The most popular electrolytes are the liquid-type ones where carbonates or esters of simple alcohol and glycol are frequently used as solvents which contain $LiPF_6$ as an electrolyte. Solvents typically are a mixed solution of ethylene carbonate (EC) of high dielectric constant and methyl ethyl carbonate (MEC) of low viscosity. Sometimes a combination of □-butyrolactone and $LiBF_4$ is utilized. Propylene carbonate is an excellent solvent, but it decomposes rapidly on the surface of graphite. If there is a short circuit, very significant heat buildup (>200° C.) can occur and ignite these types of electrolytes.

Recently, polymer electrolytes have attracted much attention because they enable freedom from electrolyte leakage and can make a thin battery. Solid-state electrolytes and some polymer electrolytes need no separator. Many kinds of polymer electrolytes have been proposed, but only a few are utilized in practical batteries. Polysiloxane is one of recent interest. Many solid polyelectrolyte types are not a true solid polymer, but a polymer gel containing liquid electrolyte as a plasticizer.

The separator has two primary functions: one is to avoid the direct contact between the anode and cathode, while it allows a free mass transfer of the electrolyte, and the other is a shutter action to stop the mass transfer in the case of accidental heat generation. The separator film melts resulting in pore closure. Biaxially orientated polyolefin film is commonly used to obtain a high porosity film.

A composite anode material made of silicon/graphite/multi-walled carbon nanotubes (MWNTs) for Li-ion batteries has been prepared by ball milling. This composite anode material showed a discharge capacity of 2274 milliamp-hours per gram (mAh/g) in the first cycle, and after 20 charge-discharge cycles, a reversible capacity of 584 mAh/g was retained, higher than 218 mAh/g for silicon/graphite composite. However, the silicon particles appeared to be on a scale of about a micrometer in diameter and were irregularly distributed. Further, no attachment of the particles to the MWNT was apparent.

Vertically-aligned multi-walled carbon nanotube (VAMWNT) electrodes grown on substrates such as aluminum or silicon have been investigated. The current state-of the-art of lithium-ion batteries utilizes graphite as a negative electrode with a maximum theoretical specific capacity of 372 mAh/g and a practical specific capacity ranging from 150-370 mAh/g, which were aligned in the direction of current flow. By aligning the nanotubes in this manner, increased access and interfacial dynamics between lithium-ions and the interstitial spaces of the MWNTs as well as the internal and external surfaces of the MWNTs were thought possible. These electrodes were able to produce a stable and reversible capacity of 650 mAh/g. As mentioned previously, fully aligned carbon nanotubes as made can still associate to form bundles and cracking is more likely along the tube lengths.

Aligned carbon nanotube coaxial nanowires have also been prepared by electrochemically depositing a concentric layer of an appropriate conducting polymer or titanium dioxide, TiO2, coating onto the individual aligned carbon nanotubes. These aligned carbon nanotube coaxial nanowires were demonstrated in the laboratory to possess unique electron transfer properties and speculated to have potential significance for a wide range of device applications, including batteries and supercapacitors.

Mats of carbon nanotubes and carbon particles have been utilized as conductive systems to replace metal foils. Impregnation of xerogels of V_2O_5 composite electrode gave a reversibility specific capacity of 160 $mAh.g^{-1}$ at a constant discharge/charge current of 95 pk $mA.g^{-1}$ between 4 and 2V versus Li/Li^+ Simple impregnation methods do not control the spatial distribution of the particles to prevent local charge density fluctuations and stable structure over time. Control of the distribution of the nanoscale particles or layers by attachment is believed to be beneficial to maintain the high crystal surface area to volume ratio.

SUMMARY OF THE INVENTION

The present disclosure, in some embodiments, relates to improved energy storage or collection devices, and more particularly to a battery, capacitor or photovoltaic that has high energy density, power density, and photon conversion efficiency having at least one of at least two electrodes containing carbon nanotubes or other types of nanotubes from elements or metal complexes that have been exfoliated from their as-synthesized state—meaning as the carbon nanotubes were originally made in the un-exfoliated state, have attached electro-or photo active nanoscale particles or layers and having a dielectric medium or electrolyte.

In another embodiment, the energy storage or collection devices contain nanotubes further associated or functionalized with electro active or photo active species containing transition elements, oxides and complexes of transition metals, such as, but not limited to Ru, Ir, W, Mo, Mn, Ni, Co, Ti, V, Si, Sn, Fe and combinations thereof.

In another embodiment, the energy storage or collection devices contain nanotubes further associated or functionalized with electro active or photoactive species containing and admixed with conducting polymers such as polyaniline or polyvinylpyrrole.

In another embodiment, the energy storage or collection devices contain exfoliated nanotubes that are dispersed using a surfactant that can also serve as an electrolyte salt, such as tetraethyl- or tetrabutylammonium tetrafluoroborate.

In yet another embodiment, the energy storage or collection devices contain nanotubes that have been exfoliated and have attached nanoscale particles or layers wherein the assembly is then oriented.

In another embodiment, the energy storage or collection devices contain nanotubes that have been exfoliated and have attached nanoscale particles or layers and then fabricated in the form of a film, thin mats, fibers, cloths, non-woven fabrics, felts and the like.

In another embodiment, the energy storage or collection devices contain at least two electrodes having at least one of the electrodes containing carbon or mineral nanotubes that have been exfoliated and having attached nanoscale particles or layers; an electrolyte disposed between the electrodes; and a separator disposed in the electrolyte to provide electrical insulation between the electrodes while allowing ion flow within the electrolyte.

In further embodiments, the energy storage or collection devices contain an insulator further having a portion of nanotubes having been exfoliated and having attached nanoscale particles or layers distributed in an insulator medium such that the dielectric constant of the insulator and nanotube mixture is greater than the insulator medium alone.

In another embodiment, methods for making an energy storage or collection device include redispersing the exfoliated nanotubes in a medium such as a polymer or viscous liquid, to create an electrode and laminating with another media to the electrode acting as a dielectric or electrolyte. Formation of the electrode may occur through coextrusion of liquids or melts through multilayer dies or multilayer generators, such as described in U.S. Pat. Nos. 3,415,920 and 5,094,793. The resultant multilayer can be stacked and connected in series to give higher voltage. Alternatively, the energy storage devices can be made with the exfoliated nanotubes by processing the mixture of the exfoliated nanotubes by solvent casting, spraying, paste spreading, compression stretching, or combinations of the like to give the desired form.

In another embodiment, the incorporation of exfoliated nanotubes to the electrode material provides enhanced strength and ruggedness to the electrode, allowing further shaping of the electrode or performance under more demanding environments such as high vibration or extreme thermal cycling. This is compared to an electrode material without exfoliated nanotubes.

DETAILED DESCRIPTION OF THE INVENTION

The present disclosure relates to improved energy storage or collection devices consisting of current collectors, electrodes, insulators, electrolytes or separators comprising exfoliated nanotubes with attached nanoscale particles or layers that are electro-or photoactive.

The nanotubes contain materials such as, but not limited to carbon, silicon, metals or inorganic compounds or mixtures thereof. The nanotubes have a diameter of between about 1 nm and about 20 nm in some embodiments and between about 1 nm and about 10 nm in other embodiments. The nanotubes have an aspect ratio, or length to diameter ratio, of least about 10 in some embodiments and at least about 60 in other embodiments. Carbon nanotubes generally have an inner diameter of about 1.2 nm.

"As-synthesized" carbon nanotubes can be made from any known means such as chemical vapor deposition laser ablation, high pressure carbon monoxide synthesis and the like. Chemical Vapor Deposition (CVD) is the most frequently employed process for the manufacture of carbon nanotubes as well as the process most predominately used by the largest suppliers in the industry. This method utilizes a carbon source in gaseous form (referred to as a precursor) being diluted with an inert gas and inflowing into the reactor. As the precursor interacts with a catalyst on the fixed substrate, the gaseous carbon sources decompose into a solid state to form a mixture of single-, dual-, and multi-walled carbon nanotubes along with other impurities in an agglomerate.

Carbon nanotubes can be oxidized using techniques such as a mixture of concentrated sulfuric acid and nitric acid for lengths of time to give a combination of hydroxyl and carboxylic acid groups on the carbon nanotube surface. These hydroxyl and carboxyl groups can be easily converted to other functional groups such as oxychlorides or fluorides as desired. The carboxyl groups are suitable for attachment of metals, metal oxides or other element-containing complexes.

Exfoliation of nanotubes means that there is no direct association with other nanotubes along substantially the length of the nanotube.

Attachment of nanoscale particles or layers means that the nanoscale particle or layer is held next to the nanotube by at least one electrostatic or covalent bonding site.

EXAMPLE

A solution of lithium hydroxide is added to a deposition of exfoliated carbon nanotubes having carboxylate functionality followed by washing with deionized water and then dried. Presynthesized orthorhombic $LiFePO_4$ nanocrystals (or other cathode material) can be attached to sidewalls of the dispersed carbon nanotubes by association with $LiCO_3$. Alternatively, $LiFePO_4$ nanocrystals can be attached directly to the exfoliated functionalized carbon nanotubes through in-situ synthesis of the inorganic crystal at temperatures 400° C. as carbon nanotubes are known to be stable at these temperatures. $LiFePO_4$ is inherently low in electrical (electronic and ionic) conductivity. By using nanosized particles Li can easily access and exit the crystal galleries thereby increasing Li charge and discharge rates. Using nanoscale crystals also mitigates problems of cracking due to expansion/contraction of the lattice as Li migrates in and out during charging/discharging. Attachment of the nanoscale electroactive species to the carbon nanotube facilitates the electron transfer and prevents local migration of nanoparticles which could lead to inhomogeneous performance.

A binder such as polyvinylidene fluoride can be added, if desired, to the nanotubes that have been exfoliated and have electro-or photoactive materials attachments. The binders can be added as a solution or melt.

Orientation of the exfoliated carbon nanotubes with attachments can be obtained by dispersing the carbon nanotubes and attachments in polymeric media and orienting the tubes by fiber extrusion. The polymeric media could be a binder such as PVDF. Other selected polymeric media could include polyethylene oxide or polyvinyl alcohol that can be incorporated within the electrolyte system or easily removed by heating at 250° C., or by washing with water.

These tubes can be functionalized with a variety of chemical groups such as Al, Ga, In, Au, and Pd, all useful as silicon nanotube catalysts. Silicon nanotubes can be grown in plasma at 400° C. on the catalyst particles on the exfoliated carbon nanotubes.

Substrate-enhanced electroless deposition (SEED) methods can be used for decorating carbon nanotubes with various metal and metal oxide nanoparticles such as Cu, Ag, Sn, Au, Pt, Pd, Zn, and V. Continued deposition of nanoparticles can lead to complete coverage of the nanotube if desired. Alternatively, a technique such as using Fehlings solution can be used to fully coat the exfoliated nanotubes with an oxide. Nanoscale particles of tin oxide, for example, attached to the exfoliated carbon nanotubes is useful as an anode in lithium ion batteries. Likewise, attached nanoscale TiO_2 particles to exfoliated carbon nanotubes are useful to provide improved photovoltaic devices.

A general procedure for making attachments of silicon to carbon surfaces (not involving MWNTs) can be found in Stewart et al., J. Am. Chem. Soc, 2004, 126:370-378. In various embodiments, silyl-protected terminal alkyne moieties are placed on the surface of the exfoliated carbon nanotubes in a uniform manner, and then nanoscale particles of silicon are added to provide a uniform distribution of silicon particles on the surface. The surfaces of commercially available silicon nanoparticles can be treated to enable stable particle dispersions in various solvents. The final structures are obtained, for example but not limited to, by combination of exfoliated carbon nanotubes and fully dispersed silicon nanoparticles in an appropriate liquid media followed by the attachment chemistry. These nanoscale particles are 3-20 nm in diameter. The attached silicon particles, tubes or layers are useful for improved anodes for lithium ion batteries as well as solar photovoltaic devices.

Likewise, attachment of silicon-oxycarbide particles to exfoliated carbon nanotubes are useful for cathodes of lithium ion batteries.

We claim:

1. An energy storage and collection device comprising:

a) at least two electrodes;

b) at least one of the electrodes containing carbon or mineral nanotubes that have been exfoliated from their as-synthesized state and have attached electroactive or photo active nanoscale particles or layers;

c) at least two current collectors, each in contact with an electrode, or the electrode also functions as the current collector; and

d) optionally an insulator.

2. An energy storage device comprising:

a) at least two electrodes;

b) at least one of the electrodes containing carbon or mineral nanotubes that have been exfoliated from their as-synthesized state and have attached electroactive or photoactive nanoscale particles or layers;

c) at least two current collectors, each in contact with an electrode, or the electrode also functions as the current collector;

d) an electrolyte disposed between said electrodes; and

e) optionally a separator disposed in said electrolyte to provide electrical insulation between the electrodes while allowing ion flow within said electrolyte.

3. The energy storage or collection device of claim **1** wherein said electrodes or current collectors contain single walled carbon nanotubes.

4. The energy storage or collection device of claim **2** wherein said electrodes or current collectors contain single walled carbon nanotubes.

5. The energy storage or collection device of claim **3** or **4**, wherein the single walled carbon nanotubes are primarily conducting.

6. The energy storage or collection device of claim **1** wherein said electrodes or current collectors contain nanotubes of length greater than about 0.2 micrometers.

7. The energy storage or collection device of claim **2** wherein said electrodes or current collectors contain nanotubes of length greater than about 0.2 micrometers.

8. The energy storage or collection device of claim **6** or **7**, wherein the carbon nanotubes have a narrower distribution of lengths after exfoliation.

9. The energy storage or collection device of claim **1**, wherein the nanotubes are more than 96 percent pure by weight.

10. The energy storage device of claim **2**, wherein said electrodes or current collectors contain nanotubes which are substantially without the impurities present after initial synthesis.

11. The energy storage or collection device of claim **1** wherein at least one of the electrodes comprising nanotubes has been contacted with a surfactant that is also an electron transfer agent.

12. The energy storage or collection device of claim **2** wherein at least one of the electrodes comprising nanotubes has been contacted with a surfactant that is also an electrolyte or electron transfer agent.

13. The energy storage or collection device of claim **1** wherein the insulator further comprises a portion of nanotubes with attached nanoscale particles or layers distributed in an insulator medium such that the dielectric constant of the insulator and nanotube mixture is greater than the insulator medium.

14. The energy storage or collection device of claim **1** wherein the carbon or mineral nanotubes within the electrode or current collector are oriented.

15. The energy storage or collection device of claim **2** wherein the carbon or mineral within the electrode or current collector are oriented.

16. The energy storage or collection device of claim **1** wherein the nanotubes are admixed with conducting polymers.

17. The energy storage or collection device of claim **2** wherein the nanotubes are admixed with conducting polymers.

18. An energy storage or collection device comprising:

a) at least two electrodes;

b) at least one of the electrodes containing carbon or mineral nanotubes that have been exfoliated from their as-synthesized state and have attached electroactive or photoactive nanoscale particles or layers; and

c) an electrolyte comprising a lithium salt and optionally an organic solvent.

19. An energy storage device of claim **18** wherein at least one electrode contains single walled carbon nanotubes, wherein a majority of the single walled carbon nanotubes are conducting.

20. The energy storage or collection device of claim **18**, wherein at least one electrode contains nanotubes of length greater than 0.02 micrometers.

21. The energy storage or collection device of claim **20**, wherein the nanotubes have a narrower distribution of lengths after exfoliation.

22. The energy storage device of claim **18** wherein the nanotubes are oriented.

23. The energy storage or collection device of claim **18** wherein the electrodes contain nanotubes which are substantially without the impurities present after initial synthesis.

24. A method for making an energy storage or collection device comprising:

dispersing exfoliated nanotubes with attached nanoscale particles or layers in a medium to create an electrode; and

joining the electrode with another media acting as a dielectric or electrolyte.

25. The method of claim **24**, wherein the joining is performed using coextrusion through multilayer dies or multilayer generators.

26. The method of claim **24** wherein the electrode and the media are assembled by casting, spraying, paste spreading, compression, or stretching to give a desired form.

27. An energy storage or collection device that comprises exfoliated nanotubes with attached nanoscale particles and layers that provides increased strength and ruggedness to the device compared to devices without exfoliated nanotubes.

* * * * *

EXHIBIT 2

US009636649B2

(12) **United States Patent**
Bosnyak et al.

(10) **Patent No.: US 9,636,649 B2**
(45) **Date of Patent: *May 2, 2017**

(54) **DISPERSIONS COMPRISING DISCRETE CARBON NANOTUBE FIBERS**

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(57) **ABSTRACT**

This present invention relates to the carbon nanotubes as composites with materials such as elastomers, thermosets and thermoplastics or aqueous dispersions of open-ended carbon nanotubes with additives. A further feature of this invention relates to the development of a concentrate of carbon nanotubes with an elastomer wherein the concentrate can be further diluted with an elastomer and other polymers and fillers using conventional melt mixing equipment.

23 Claims, No Drawings

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DISPERSIONS COMPRISING DISCRETE CARBON NANOTUBE FIBERS

CROSS-REFERENCES

This application is a continuation-in-part application of U.S. Ser. No. 15/225,215 filed Aug. 1, 2016 and allowed Sep. 12, 2016 which was a continuation-in-part application of U.S. Ser. No. 15/166,931 filed May 27, 2016 and issued as U.S. Pat. No. 9,422,413 which was a continuation of U.S. Ser. No. 14/924,246, filed Oct. 27, 2015 and issued as U.S. Pat. No. 9,353,240, which is a continuation of U.S. Ser. No. 13/993,206, filed Jun. 11, 2013 and issued as U.S. Pat. No. 9,212,273, which claims priority to PCT/EP2011/072427, filed Dec. 12, 2011, which claims benefit of U.S. provisional application 61/423,033, filed Dec. 14, 2010. This application is also related to U.S. Ser. Nos. 62/319,599; 14/585,730; 14/628,248; and Ser. No. 14/963,845.

FIELD OF INVENTION

The present invention is directed to novel compositions and methods for producing elastomer composite blends with discrete carbon nanotubes.

BACKGROUND OF THE INVENTION

Carbon nanotubes can be classified by the number of walls in the tube, single-wall, double wall and multiwall. Each wall of a carbon nanotube can be further classified into chiral or non-chiral forms. Carbon nanotubes are currently manufactured as agglomerated nanotube balls or bundles. Use of carbon nanotubes as a reinforcing agent in polymer composites is an area in which carbon nanotubes are predicted to have significant utility. However, utilization of carbon nanotubes in these applications has been hampered due to the general inability to reliably produce individualized carbon nanotubes. To reach the full potential of performance enhancement of carbon nanotubes as composites in polymers the aspect ratio, that is length to diameter ratio, should be substantially greater than 40. The maximum aspect ratio for a given tube length is reached when each tube is fully separated from another. A bundle of carbon nanotubes, for example, has an effective aspect ratio in composites of the average length of the bundle divided by the bundle diameter.

Various methods have been developed to debundle or disentangle carbon nanotubes in solution. For example, carbon nanotubes may be shortened extensively by aggressive oxidative means and then dispersed as individual nanotubes in dilute solution. These tubes have low aspect ratios not suitable for high strength composite materials. Carbon nanotubes may also be dispersed in very dilute solution as individuals by sonication in the presence of a surfactant. Illustrative surfactants used for dispersing carbon nanotubes in aqueous solution include, for example, sodium dodecyl sulfate, or cetyltrimethyl ammonium bromide. In some instances, solutions of individualized carbon nanotubes may be prepared from polymer-wrapped carbon nanotubes. Individualized single-wall carbon nanotube solutions have also been prepared in very dilute solutions using polysaccharides, polypeptides, water-soluble polymers, nucleic acids, DNA, polynucleotides, polyimides, and polyvinylpyrrolidone. The dilution ranges are often in the mg/liter ranges and not suitable for commercial usage.

SUMMARY OF THE INVENTION

The present invention relates to a composition comprising a plurality of discrete carbon nanotube fibers having an aspect ratio of from about 25 to about 500, and at least one natural or synthetic elastomer, and optionally at least one filler. The composition can have carbon nanotube fibers with an oxidation level of from about 3 weight percent to about 15 weight percent, or from about 0.5 weight percent up to about 4, or up to about 3, or up to 2 weight percent based on the total weight of discrete carbon nanotubes. The carbon nanotube fibers comprise preferably of about 1 weight percent to about 30 weight percent of the composition and the composition is in the form of free flowing particles or a bale. The composition is further comprising of at least one surfactant or dispersing aid. The composition can comprise the natural or synthetic elastomer selected from the group consisting of, but not limited to, natural rubbers, polyisobutylene, polybutadiene and styrene-butadiene rubber, butyl rubber, polyisoprene, styrene-isoprene rubbers, styrene-isoprene rubbers, ethylene propylene diene rubbers, silicones, polyurethanes, polyester-polyethers, hydrogenated and non-hydrogenated nitrile rubbers, halogen modified elastomers, flouro-elastomers, and combinations thereof. The composition contains fibers that are not entangled as a mass and are uniformly dispersed in the elastomer.

In another embodiment, the invention is a process to form a carbon nanotube fiber/elastomer composite comprising the steps of: (a) selecting discrete carbon nanotube fibers having an aspect ratio of from 25 to 500, (b) blending the fibers with a liquid to form a liquid/fiber mixture, (c) optionally adjusting the pH to a desired level, (d) agitating the mixture to a degree sufficient to disperse the fibers to form a dispersed fiber mixture, (e) optionally combining the dispersed fiber mixture with at least one surfactant, (f) combining the dispersed fiber mixture with at least one elastomer at a temperature sufficient to incorporate the dispersed fiber mixture to form a carbon nanotube fiber/elastomer composite/liquid mixture, (g) isolating the resulting carbon nanotube fiber/elastomer composite from the liquid. The carbon nanotube fibers comprise from about 1 to about 30 weight percent of the fiber/elastomer composite of (g). The liquid is aqueous based. The agitating step (d) comprises sonication. In this embodiment, the elastomer is selected from, but not limited to, the natural or synthetic elastomer selected from the group consisting of, but not limited to, natural rubbers, polyisobutylene, polybutadiene and styrene-butadiene rubber, butyl rubber, polyisoprene, styrene-isoprene rubbers, styrene-isoprene rubbers, ethylene propylene diene rubbers, silicones, polyurethanes, polyester-polyethers, hydrogenated and non-hydrogenated nitrile rubbers, halogen modified elastomers, fluoro-elastomers, and combinations thereof. The composition is further comprising sufficient natural or synthetic elastomer to form a formulation comprising from about 0.1 to about 25 weight percent carbon nanotube fibers.

In another embodiment, the invention is a formulation in the form of a molded or fabricated article, such as a tire, a hose, a belt, a seal and a tank track pad, wheel, bushings or backer plate components.

In another embodiment, the invention is a nanotubes/elastomer composite further comprising of filler or fillers such as carbon black and/or silica, and wherein a molded film comprising the composition has a tensile modulus at 5 percent strain of at least about 12 MPa. The composition comprising of carbon black, and wherein a molded film comprising the composition has a tear property of at least about 0.8 MPa.

In yet another embodiment of the invention is a carbon nanotube/elastomer composition further comprising of filler, and where in a molded film comprising the composition has a tensile modulus at 5% strain of at least 8 MPa.

In yet another embodiment of the invention is a carbon nanotube fiber/elastomer composite, wherein the carbon nanotube fibers are discrete fibers and comprise from about 10 to about 20 weight percent fibers and wherein the elastomer comprises a styrene copolymer rubber.

In still another embodiment of the invention is a method for obtaining individually dispersed carbon nanotubes in rubbers and/or elastomers comprising (a) forming a solution of exfoliated carbon nanotubes at pH greater than or equal to about 7, (b) adding the solution to a rubber or elastomer latex to form a mixture at pH greater than or equal to about 7, (c) coagulating the mixture to form a concentrate, (d) optionally incorporating other fillers into the concentrate, and (e) melt-mixing said concentrate into rubbers and/or elastomers to form elastomeric composites. In this embodiment the carbon nanotubes comprise less than or equal to about 2 percent by weight of the solution. A further embodiment is that the coagulation step comprises mixing with acetone. In another embodiment, the coagulation step comprises drying the mixture. In yet another embodiment the coagulation step comprises adding at least one acid to the mixture at pH less than or equal to about 4.5 together with at least one monovalent inorganic salt. In another embodiment, the mixture has divalent or multivalent metal ion content of less than about 20,000 parts per million, preferably less than about 10,000 parts per million and most preferably less than about 1,000 parts per million.

Another aspect of this invention are coagulating methods/agents are those that enable the carbon nanotube to be non-ordered on the surface of the elastomer latex particle and together are substantially removable from the liquid mixture. A further aspect of this invention is a method to reduce or remove surfactants in the latex/carbon nanotube fiber composite system organic molecules of high water solubility such as acetone, denatured alcohol, ethyl alcohol, methanol, acetic acid, tetrahydrofuran. Another aspect of this invention is to select coagulating methods that retain surfactant in the latex/carbon nanotube fiber material which includes coagulating methods such as sulfuric acid and inorganic monovalent element salt mixtures, acetic acid and monovalent element salt mixtures, formic acid and inorganic monovalent element salt mixtures, air drying, air spraying, steam stripping and high speed mechanical agitation.

Yet another embodiment of the invention is an individually dispersed carbon nanotube/rubber or carbon nanotube/elastomer concentrate comprising free flowing particles or a bale. A further aspect of this invention is an individually dispersed carbon nanotube/rubber or carbon nanotube/elastomer concentrate comprising free flowing particles or a bale wherein the concentrate contains a concentration of less than 20,000 parts per million of divalent or multivalent metal salt.

Another embodiment of the invention is an individually dispersed carbon nanotube/rubber or carbon nanotube/elastomer concentrate comprising free flowing particles or a bale wherein the concentrate contains agglomerations of carbon nanotubes that comprise less than 1 percent by weight of the concentrate and wherein the carbon nanotube agglomerates comprise more than 10 microns in diameter. An embodiment of the invention is a composite comprising the concentrate.

In another embodiment, the elastomer nanotube fiber composition, particularly materials made from elastomers commonly called either natural or synthetic rubber or rubber compounds (with the addition of fillers such as carbon or silicon) includes wherein the fiber surface modifier or surfactant is chemically or physically (or both) bonded to the elastomer and/or the isolated fibers or the filler in the compounds.

In another embodiment, the material-nanotube fiber composition includes wherein the fiber surface modifier or surfactant is chemically bonded to the material and/or fiber. As an example, oleylamine (1-amino-9-octadecene) can be reacted with carbon nanotubes containing carboxylic groups to give the amide. On addition of the amide modified carbon nanotube fiber to a vinyl containing polymer material such as styrene-butadiene followed by addition of crosslinking agents comprising such as peroxides or sulfur, the vinyl containing polymer can be covalently bonded to the amide functionality of the carbon nanotube.

In one embodiment of this invention a method is disclosed in which the elastomer/carbon nanotube concentrate is dispersed first into another elastomer or thermoplastic to a uniform consistency before addition of other additives such as other fillers and additives, including carbon black, silica, graphene, oils and antioxidants.

Another embodiment of this invention is a method of mixing carbon nanotubes and at least one first elastomer, wherein a master batch of carbon nanotubes is first melt mixed with the elastomer, either the same or different from the first elastomer, at a temperature from about 20 to about 200° C., subsequently then additional elastomers, fillers, and additives are added and melt mixed further, to produce a composition suitable for vulcanization. A solvent can be added to facilitate mixing which can be removed after the at least one first elastomer, wherein a master batch of carbon nanotubes is first mixed with the elastomer, or after all ingredient are added and mixed.

The exfoliated carbon nanotube fibers of this invention impart significant strength and stiffness to the materials. These new elastomer nanotube filler materials can improve the frictional, adhesive, cohesive, noise and vibration, rolling resistance, tear, wear, fatigue and crack resistance, hysteresis, large strain effects (Mullins effect), small strain effects (Payne effect) and oscillation or frequency properties and swelling resistance to oil of the elastomers and elastomer compounds. This change in properties will be beneficial for applications such as tires or other fabricated rubber or rubber compounded parts.

For a more complete understanding of the present disclosure, and the advantages thereof, reference is now made to the following descriptions describing specific embodiments of the disclosure.

DETAILED DESCRIPTION OF THE INVENTION

In the following description, certain details are set forth such as specific quantities, sizes, etc., so as to provide a thorough understanding of the present embodiments disclosed herein. However, it will be evident to those of ordinary skill in the art that the present disclosure may be practiced without such specific details. In many cases, details concerning such considerations and the like have been omitted inasmuch as such details are not necessary to obtain a complete understanding of the present disclosure and are within the skills of persons of ordinary skill in the relevant art.

While most of the terms used herein will be recognizable to those of ordinary skill in the art, it should be understood, however, that when not explicitly defined, terms should be interpreted as adopting a meaning presently accepted by those of ordinary skill in the art. In cases where the construction of a term would render it meaningless or essentially meaningless, the definition should be taken from Webster's Dictionary, 3rd Edition, 2009. Definitions and/or interpretations should not be incorporated from other patent applications, patents, or publications, related or not, unless specifically stated in this specification or if the incorporation is necessary for maintaining validity.

Functionalized carbon nanotubes of the present disclosure generally refer to the chemical modification of any of the carbon nanotube types described hereinabove. Such modifications can involve the nanotube ends, sidewalls, or both. Chemical modifications may include, but are not limited to covalent bonding, ionic bonding, chemisorption, intercalation, surfactant interactions, polymer wrapping, cutting, solvation, and combinations thereof. In some embodiments, the carbon nanotubes may be functionalized before, during and after being exfoliated.

In various embodiments, a plurality of carbon nanotubes is disclosed comprising single wall, double wall or multi wall carbon nanotube fibers having an aspect ratio of from about 25 to about 500, preferably from about 60 to about 200, and a oxidation level of from about 3 weight percent to about 15 weight percent, preferably from about 5 weight percent to about 10 weight percent. The oxidation level is defined as the amount by weight of oxygenated species covalently bound to the carbon nanotube. The thermogravimetric method for the determination of the percent weight of oxygenated species on the carbon nanotube involves taking about 5 mg of the dried oxidized carbon nanotube and heating at 5° C./minute from room temperature to 1000 degrees centigrade in a dry nitrogen atmosphere. The percentage weight loss from 200 to 600 degrees centigrade is taken as the percent weight loss of oxygenated species. The oxygenated species can also be quantified using fourier transform infra-red spectroscopy, FTIR, particularly in the wavelength range 1730-1680 cm^{-1}.

The carbon nanotube fibers can have oxidation species comprising of carboxylic acid or derivative carbonyl containing species and are essentially discrete individual fibers, not entangled as a mass. The derivative carbonyl species can include ketones, quaternary amines, amides, esters, acyl halogens, monovalent metal salts and the like. Alternatively or in addition, the carbon nanotubes may comprise an oxidation species selected from hydroxyl or derived from hydroxyl containing species.

As-made carbon nanotubes using metal catalysts such as iron, aluminum or cobalt can retain a significant amount of the catalyst associated or entrapped within the carbon nanotube, as much as five weight percent or more. These residual metals can be deleterious in such applications as electronic devices because of enhanced corrosion or can interfere with the vulcanization process in curing elastomer composites. Furthermore, these divalent or multivalent metal ions can associate with carboxylic acid groups on the carbon nanotube and interfere with the discretization of the carbon nanotubes in subsequent dispersion processes. In other embodiments, the oxidized fibers comprise a residual metal concentration of less than about 10000 parts per million, ppm, and preferably less than about 1000 parts per million. The metals can be conveniently determined using energy dispersive X-ray, EDX.

In another embodiment, a mixture of master batches using different rubbers added to blends of different rubbers used in the rubber compound such that each rubber has a master batch that is compatible so that the individually dispersed nanotubes are distributed whether uniformly or non-uniformly in each rubber domain. This is sometimes necessary so that blends of rubbers used in the rubber compound will have carbon nanotubes in each rubber component.

An illustrative process for producing discrete oxidized carbon nanotubes follows: 3 liters of sulfuric acid, 97 percent sulfuric acid and 3 percent water, and 1 liter of concentrated nitric acid containing 70 percent nitric acid and 3 percent water, are added into a 10 liter temperature controlled reaction vessel fitted with a sonicator and stirrer. 40 grams of non-discrete carbon nanotubes, grade Flowtube 9000 from CNano corporation, are loaded into the reactor vessel while stirring the acid mixture and the temperature maintained at 30° C. The sonicator power is set at 130-150 watts and the reaction is continued for three hours. After 3 hours the viscous solution is transferred to a filter with a 5 micron filter mesh and much of the acid mixture removed by filtering using a 100 psi pressure. The filter cake is washed one times with four liters of deionized water followed by one wash of four liters of an ammonium hydroxide solution at pH greater than 9 and then two more washes with four liters of deionized water. The resultant pH of the final wash is 4.5. A small sample of the filter cake is dried in vacuum at 100° C. for four hours and a thermogravimetric analysis taken as described previously. The amount of oxidized species on the fiber is 8 percent weight and the average aspect ratio as determined by scanning electron microscopy to be 60.

The discrete oxidized carbon nanotubes (CNT) in wet form are added to water to form a concentration by weight of 1 percent and the pH is adjusted to 9 using ammonium hydroxide. Sodium dodecylbenzene sulfonic acid and is added at a concentration 1.25 times the mass of oxidized carbon nanotubes. The solution is sonicated while stirring until the CNT are fully dispersed in the solution. Full dispersion of individual tubes is defined when the UV absorption at 500 nm is above 1.2 absorption units for a concentration of 2.5×10^{-5} g CNT/ml. Latex SBR LPF 5356 (Goodyear Rubber Company) with a solids SBR concentration of 70.2% (by weight) was added to the CNT solution such that the solids ratio is 10 parts CNT for 90 parts SBR by weight.

Sulfuric acid is then added sufficient to bring the pH to 2 and sodium chloride added at a ratio of 50 g/liter of fluid while stirring. Stirring continues for 10 minutes then the coagulant is removed by filtering. The filtrate is a clear liquid. The coagulant is dried in a vacuum oven at 40° C. overnight.

Preparation of Aqueous Dispersions Comprising Additives According to the Present Invention

As described above and below, various additives may be employed in the aqueous dispersions of discrete, multi-wall oxidized carbon nanotubes. If desired, the carbon nanotubes may be open on at least one or both ends. In this manner at least a portion of the additives that are appropriate in size may be contained in the interior of the discrete multi-wall carbon nanotubes. Typically, the average diameter of the multi-wall nanotube opening is larger than the hydrodynamic radius of the additive molecules to be contained within the interior of the discrete, multi-wall oxidized carbon nanotubes. Such average diameters of the multi-wall nanotube opening will vary by specific carbon nanotubes but may be at least about 1, or at least about 3, up to about 15, or up to about 8 nanometers. Typically, representative additive molecules that fit within representative discrete, multi-wall oxidized carbon nanotubes are less than 50,000 Daltons, or less than 40,000, or less than 30,000, or less than 25,000, or less than 20,000 or even less than 17,000 Daltons.

Such additives may include, for example, various surfactants or dispersing aids and compounds such as sodium dodecyl sulfate, cetyltrimethyl ammonium bromide, polyvinyl alcohol, polyalkylene oxide such as polyethylene oxide, cellulosics such as carboxymethyl cellulose, polyacids such as polyglycolic acid, polyacrylic acid, and polylactic acid, polyvinylpyrrolidone, various peptides and amino acids, as well as proteins, polysaccharides, combinations thereof and the like. Other additives include, for example, drugs, proteins and compounds such as those described in US 2009/0170768 to Tour et al. which is incorporated herein by reference. Exemplary additives include, for example, a drug molecule, a protein molecule, and combinations thereof. Compounds such as a radiotracer molecule, a radiotherapy molecule, a diagnostic imaging molecule, a fluorescent tracer molecule, and combinations thereof may also be added. And as described in Tour US 2009/0170768 others may "include, but are not limited to, proton pump inhibitors, H2-receptor antagonists, cytoprotectants, prostaglandin analogues, beta blockers, calcium channel blockers, diuretics, cardiac glycosides, antiarrhythmics, antianginals, vasoconstrictors, vasodilators, ACE inhibitors, angiotensin receptor blockers, alpha blockers, anticoagulants, antiplatelet drugs, fibrinolytics, hypolipidemic agents, statins, hypnotics, antipsychotics, antidepressants, monoamine oxidase inhibitors, selective serotonin reuptake inhibitors, antiemetics, anticonvulsants, anxiolytic, barbiturates, stimulants, amphetamines, benzodiazepines, dopamine antagonists, antihistamines, cholinergics, anticholinergics, emetics, cannabinoids, 5-HT antagonists, NSAIDs, opioids. bronchodilator, antiallergics, mucolytics, corticosteroids, beta-receptor antagonists, anticholinergics, steroids, androgens, antiandrogens, growth hormones, thyroid hormones, anti-thyroid drugs, vasopressin analogues, antibiotics, antifungals, antituberculous drugs, antimalarials, antiviral drugs, antiprotozoal drugs, radioprotectants, chemotherapy drugs, cytostatic drugs, and cytotoxic drugs. In various embodiments of the compositions, the at least one type of payload molecule comprises paclitaxel."

Such additives may include, for example, dicarboxylic/tricarboxylic esters, timellitates, adipates, sebacates, maleates, glycols and polyethers, polymeric plasticizers, bio-based plasticizers, and mixtures thereof. In other embodiments such additives may include, for example, a process oil such as, for example, a process oil selected from the group consisting of naphthenic oils, paraffin oils, paraben oils, aromatic oils, vegetable oils, seed oils, silicones, and mixtures thereof. In other embodiments such additives may include, for example, a solvent such as substituted or unsubstituted, halogenated or nonhalogenated hydrocarbons. Such solvents may include, for example, xylene, pentane, methylethyl ketone, hexane, heptane, ethyl acetate, ethers, carbonates, dicloromethane, dichloroethane, cyclohexane, chloroform, carbon tetrachloride, butyl acetate butanol, benzene, alcohols, and mixtures thereof. In other embodiments such additives may include, for example, at least one reactive species capable of creating a thermoset polymer such as, for example, epoxy, polyurethane, silicone, and mixtures thereof. In other embodiments such additives may include, for example, a natural wax, synthetic wax, or a mixture thereof. Such waxes may include, for example, plant derived, animal derived, petroleum derived, polyethylene derived and other related derivatives. Such waxes may also further comprise such additives as, for example, a fluoroelastomer. In other embodiments such additives may include, for example, at least one filler. Such fillers may include, for example, a filler selected from silicon, lead, lead derivatives, carbon black, graphite, graphene, graphene oxides, paramagnetic particles and mixtures thereof. In some embodiments the filler may have at least one dimension less than about 20 microns. Such fillers may comprise particles of any shape, for example, plates, fibers, cubes, rhomboids, spherical, and combinations thereof.

The amount of additive to be included with the dispersion (aqueous or non-aqueous) or other composition of discrete, multi-wall oxidized carbon nanotubes will vary depending upon the specific additive, the specific carbon nanotubes, desired effect, and other parameters. Typically, the amount of additive is such that greater than about 10, or greater than about 20, or greater than about 25, or greater than about 30, or greater than about 40, or greater than about 50, or greater than about 55, or greater than about 60, or greater than about 70, or greater than about 80, or greater than about 99 weight percent of the additive is within the interior of the discrete, multi-wall oxidized carbon nanotubes that are open on at least one or both ends based on the total weight of additive in the composition or dispersion. Similarly, the weight percent of nanotubes in the dispersion or composition is often low based on the total weight of the dispersion or composition, e.g., from about 0.01, or 0.1, or 0.3, or 0.5, or 0.6 up to about 30, or 15, or 10, or 5 or 3, or 1 weight percent. In some embodiments such as, for example, when an additive is wax, oil, or mixtures, the weight percent of nanotubes in the dispersion or composition may be from about 15, or from about 18 up to about 25, or 22% by weight based on the total weight of dispersion or composition. Advantageously, such dispersions or compositions may be in the form of, for example, free flowing particles.

Preparation of the Vulcanizable Composition According to the Present Invention:

A further object of the invention resides in the preparation of the vulcanizable compositions, wherein the elastomer, the concentrate of carbon-nanotubes in an elastomer composition and the cross-linking agent and optionally any of the other ingredients of the composition are mixed together. Typically the mixing is performed at an elevated temperature that may range from about 20° C. to about 200° C. The mixing may further be performed in the presence of a solvent which is then removed after mixing.

Normally the mixing time does not exceed one hour and a time in the range from 2 to 30 minutes is usually adequate.

The mixing is suitably carried out in a blending apparatus, e.g. an internal mixer such as a Banbury mixer, or a Haake or Brabender miniature internal mixer. A two roll mill mixer also provides a good dispersion of the carbon-nanotubes as well as of the other optional additives within the elastomer. An extruder also provides good mixing, and permits shorter mixing times. It is possible to carry out the mixing in two of more stages, and the mixing can be done in different apparatus, for example one stage in an internal mixer and one stage in an extruder. However, it should be taken care that no unwanted pre-crosslinking (=scorch) occurs during the mixing stage.

The compounding and vulcanization may be performed as known to any artisan (see e.g. Encyclopedia of Polymer Science and Engineering, Vol. 4, p. 66 et seq. (Compounding) and Vol. 17, p. 666 et seq. (Vulcanization)). Typically such vulcanization is performed at a temperature in the range of from 100 to 200° C., preferably 130 to 180° C. In one embodiment the preparation of a polymer vulcanizate comprises subjecting the inventive composition to a vulcanization during injection or extrusion molding.

Following is an example using styrene butadiene as an elastomer with addition of carbon nanotubes of this invention.

Example 1

The SBR concentrate is melt mixed with additional SBR (Lanxess VSL-5052-0HM) to give a final CNT concentration of 2 percent weight in a Brabender mixer by the following procedure. The temperature of the barrel is set to 115° C. The SBR and master batch is introduced into the barrel at a speed of 20-30 rpm. The speed is then increased to 50 rpm. Barrel temperature should reach 125° C. When the torque has reached a constant value, the speed is decreased to 5 rpm and the temperature controller is turned off. When the temperature in the barrel is 95° C., the speed is increased to 50 rpm. The cure package is added and mixing continues for 5 minutes. The cure package consists of sulfur 3.5 parts per hundred resin, phr, tetrabutylbenzothiozolsulfonamide 0.75 phr, diphenylguanidine 0.5 phr, stearic acid 1.5 phr, N-(1,3 Dimethylbutyl) N'-phenyl-p-phenyldiamine 2 phr and zinc oxide 3 phr.

A comparative 1 is made as above with the exception that no SBR concentrate is added.

The mixture is then cured under the following procedure using a compression molder. The platten temperature is set to 160° C., the curing overall time to 20 minutes and the water cooling time to 5 minutes. A mass of 40.6 g of rubber sample is cut into small ¼" pieces and placed in the center of mold window such that it forms a square, occupying ⅔ of the space. Foil sheets are used between sample and compression plates. Mold release is only used on the mold frame. The sample is compressed with pressure less than 10 psi for 2 minutes. Then, the pressure is increased to 25 tons and kept constant for the remaining curing cycle.

After curing the films are tested in tension at 25° C. using a tensile tester with an initial strain rate of $1\times10^{-2}s^{-1}$. Engineering Stress is the load divided by the initial cross-sectional area of the specimen. Strain is defined as the distance traversed by the crosshead of the instrument divided by the initial distance between the grips. The 100% modulus is that value of tensile stress at 100% strain. The films are also tested for work done to completely tear the specimen by introducing a razor edge notch of dimension one half the width and perpendicular to the length of the specimen to a tensile specimen.

TABLE 1

Tensile properties of cured SBR without carbon nanotubes (Comp. Ex. 1) and SBR with discrete carbon nanotubes (Ex. 1)

Sample	Tensile Strength (MPa)	100% Modulus (MPa)	Work done to Tear (MPa)
Comparative 1 SBR	1.1	0.51	0.46
Example 1 SBR + 2% wt CNT	2.26	0.8	0.79

Seen in Table 1, significant improvements in the values of tensile strength, 100% modulus and work done to tear are gained using 2 percent weight of the carbon nanotubes of this invention. These attributes are important elements that will lead to improved wear in elastomer composites.

In another aspect of this invention is a preferred method of mixing that results in improved properties wherein the master batch of carbon nanotubes is first melt mixed with another elastomer then additional rubbers, fillers and additives are added and melt mixed further to produce a composition suitable for vulcanization.

Following is an Example of Preferred Mixing

A comparative example 2 is produced using 3 phr carbon nanotubes of this invention, and carbon black filled rubber system consisting of 3 melt passes. The first pass was to mix the rubber components 60 phr styrene butadiene, SBR Lanxess VSL-5025-0HM and 40 phr Natural Rubber CB 60 grade, and an SBR-carbon nanotubes master batch containing 10 weight percent carbon nanotubes at about 160° C. The second pass was to mix into the first pass products 50 phr carbon black, type N330, 5 phr processing oil Sundex 8125, 1 phr antioxidant 6 PPD Santoflex, 3 phr zinc oxide and 3 phr stearic acid at about 160° C. The third pass was to mix in the sulfur curing compounds 1.5 phr sulfur and 1.3 phr TBBS at about 110° C. Each pass was performed with a fill factor of 75% using a Brabender mixer.

Example 2

The improved mixing approach is the same as the control except the first pass is mixing the SBR with the carbon nanotubes master batch for 5 minutes at about 170° C. followed by adding the natural rubber at about 160° C. and melt mixing for a further 5 minutes.

The results of testing the materials after curing for 8 minutes at about 160° C. are provided in Table 2. The tear initiation and total tear energy are determined from tear specimen ASTM D624-C.

TABLE 2

	Comparative 2	Example 2
Tensile Stress at Break (MPa)	18.8	20.6
Tensile Elongation to Break %	500	520
Tear Initiation Energy (MPa)	2.9	3.7
Total Tear Energy (MPa)	3.3	4.2

The above table 2 shows that the example of the invention (prediluted master batch with specific mixing) obtains improved tensile stress at break at over 1.7 MPa, improved tear initiation energy at over 0.7 MPa and including improved total tear energy at over 0.8 MPa versus the comparative example comprising different mixing techniques, proving the utility and inventiveness of the compositions of the invention.

Embodiments

1. A composition comprising a plurality of discrete carbon nanotube fibers having an aspect ratio of from about 25 to about 500, and at least one natural or synthetic elastomer, and optionally at least one filler.

2. The composition of embodiment 1 wherein at least 70 percent, preferably at least 80 percent, by weight of the nanotube fibers are fully exfoliated.

3. The composition of embodiment 1 wherein the nanotube fibers are further functionalized.

4. The composition of embodiment 1 wherein the carbon nanotube fibers comprise an oxidation level from about 3 weight percent to about 15 weight percent.

5. The composition of embodiment 1 wherein the carbon nanotube fibers comprise from about 1 weight percent to about 30 weight percent of the composition.

6. The composition of embodiment 1 in the form of free flowing particles.

7. The composition of embodiment 1 further comprising at least one surfactant or dispersing aid.

8. The composition of embodiment 1 wherein the natural or synthetic elastomer is selected from the group consisting of natural rubbers, polyisobutylene, polybutadiene and styrene-butadiene, butyl rubber, polyisoprene, ethylene propylene diene rubbers and hydrogenated and non-hydrogenated nitrile rubbers, polyurethanes, polyethers, silicones, halogen modified elastomers, especially chloroprene and fluoroelastomers and combinations thereof.

9. The composition of embodiment 1 wherein the fibers are not entangled as a mass.

10. A process to form a carbon nanotube fiber/elastomer composite comprising the steps of:

(a) selecting discrete carbon nanotube fibers having an aspect ratio of from 25 to 500,
(b) blending the fibers with a liquid to form a liquid/fiber mixture,
(c) optionally adjusting the pH to a desired level,
(d) agitating the mixture to a degree sufficient to disperse the fibers to form a dispersed fiber mixture,
(e) optionally combining the dispersed fiber mixture with at least one surfactant,
(f) combining the dispersed fiber mixture with at least one elastomer at a temperature sufficient to incorporate the dispersed fiber mixture to form a carbon nanotube fiber/elastomer composite/liquid mixture,
(g) isolating the resulting carbon nanotube fiber/elastomer composite from the liquid.

11. The process of embodiment 10 wherein the carbon nanotube fibers comprise from about 1 to about 30 weight percent of the fiber/elastomer composite of (g).

12. The process of embodiment 10 wherein the liquid is aqueous based.

13. The process of embodiment 10 wherein the agitating step (d) comprises sonication.

14. The process of embodiment 10 wherein the elastomer is selected from the group consisting of natural rubbers, polyisobutylene, polybutadiene and styrene-butadiene rubber, ethylene propylene diene rubbers, butyl rubber, polyisoprene and hydrogenated and non-hydrogenated nitrile rubbers, polyurethanes, polyethers, halogen containing elastomers and fluoroelastomers and combinations thereof.

15. The composition of embodiment 1 further comprising sufficient natural or synthetic elastomer to form a formulation comprising from about 0.1 to about 25 weight percent carbon nanotube fibers.

16. The composition of embodiment 1 in the form of a molded or fabricated article, such as a tire, a hose, a belt, a seal and a tank track.

17. The composition of embodiment 1 further comprising carbon black and/or silica and wherein a molded film comprising the composition has a tensile modulus at 5% strain and 25 degrees C. of at least about 12 MPa.

18. The composition of embodiment 1 further comprising carbon black and/or silica, and wherein a molded film comprising the composition has a tear property at 25 degrees C. of at least about 0.8 MPa.

19. The composition of embodiment 1 further comprising filler, and wherein a molded film comprising the composition has a tensile modulus at 5% strain and 25 degrees C. of at least about 8 MPa.

20. A carbon nanotube fiber/elastomer composite, wherein the carbon nanotube fibers are discrete fibers and comprise from about 10 to about 20 weight percent fibers and wherein the elastomer comprises a styrene copolymer rubber.

21. A method for obtaining individually dispersed carbon nanotubes in rubbers and/or elastomers comprising (a) forming a solution of exfoliated carbon nanotubes at pH greater than or equal to about 7, (b) adding the solution to a rubber or elastomer latex to form a mixture at pH greater than or equal to about 7, (c) coagulating the mixture to form a concentrate, (d) optionally incorporating other fillers into the concentrate, and (e) melt-mixing said concentrate into rubbers and/or elastomers to form elastomeric composites.

22. The method of embodiment 21 wherein the carbon nanotubes comprise less than or equal to about 2% wt of the solution.

23. The method of embodiment 21 wherein the coagulation step (c) comprises mixing with organic molecules of high water solubility such as acetone, denatured alcohol, ethyl alcohol, methanol, acetic acid, tetrahydrofuran that partially or wholly removes surfactants form the latex/carbon nanotube fiber concentrate.

24. The method of embodiment 21 wherein the coagulation step (c) comprises drying, steam stripping or mechanical agitation of the mixture to fully retain surfactants from the latex/carbon nanotube fiber concentrate.

25. The method of embodiment 21 wherein the coagulation step (c) comprises adding a polymeric coagulating agent, preferably polyethylene oxide.

26. The method of embodiment 21 wherein the coagulation step (c) comprises adding at least one acid to the mixture at pH less than or equal to about 4.5 together with at least one monovalent inorganic salt to retain surfactants from the latex/carbon nanotube fiber concentrate.

27. The method of embodiment 21 wherein the mixture or concentrate has a divalent or multivalent metal ion content of less than about 20,000 parts per million.

28. The method of embodiment 21 wherein the mixture or concentrate has a divalent or multivalent metal ion content of less than about 10,000 parts per million.

29. The method of embodiment 21 wherein the mixture or concentrate has a divalent or multivalent metal ion content of less than about 1,000 parts per million.

30. The method of embodiment 21 wherein the coagulation step (c) is such that agglomerations of carbon nanotubes comprise less than 1 percent weight of the concentrate and wherein the carbon nanotube agglomerates comprise more than 10 microns in diameter.

31. An individually dispersed carbon nanotube/rubber or carbon nanotube/elastomer concentrate comprising free flowing particles wherein the concentrate contains a concentration of less than 20,000 parts per million divalent or multivalent metal salt.

32. An individually dispersed carbon nanotube/rubber or carbon nanotube/elastomer concentrate comprising free flowing particles wherein the concentrate contains agglomerations of carbon nanotubes that comprise less than 1 percent by weight of the concentrate and wherein the carbon nanotube agglomerates comprise more than 10 micrometers in diameter.

33. A composite comprising the concentrate of embodiments 31 or 32.

34. A method of dispersing the individually dispersed carbon nanotube/rubber or carbon nanotube/elastomer concentrate into an elastomer by first melt mixing the elastomer and concentrate to a uniform consistency before addition of other fillers and oils.

35. The composition of embodiment 5 comprising a mixture of natural and synthetic elastomers such that each elastomer is compatible with at least one of the elastomers such that the nanotubes are individually dispersed in the mixture of elastomer(s).

36. The composition of embodiment 35 wherein at least one of the elastomers does not comprise nanotubes.

37. A composition comprising one first elastomer and nanotubes, another different second elastomer and nanotubes, and yet another third elastomer which does not comprise nanotubes.

38. A process to increase cure rate of a composition comprising at least one natural or synthetic elastomer and carbon nanotubes, comprising selecting discrete carbon nanotubes to form the cured composition, wherein the cured composition has at least a 25 percent curing rate increase over the curing rate obtained for a cured elastomer not comprising carbon nanotubes.

39. A composition of (A) elastomers, fillers and discrete carbon nanotubes wherein to maintain or increase stiffness or hardness as compared to (B) a composition not containing discrete carbon nanotubes, wherein composition (A) has less filler content than (B).

40. A composition of embodiment 39 wherein 1× parts per hundred elastomer discrete carbon nanotube of composition (A) replaces 5× parts per hundred elastomer or more of the non-carbon nanotube filler of composition (B), where x is 0.1-15.

41. A method of mixing carbon nanotubes and at least one first elastomer, wherein a master batch of carbon nanotubes is first melt mixed with the elastomer, either the same or different from the first elastomer, at a temperature from about 20 to about 200° C., subsequently then additional elastomers, fillers, and additives are added and melt mixed further, to produce a composition suitable for vulcanization.

42. A method of mixing carbon nanotubes and at least one first elastomer, wherein a master batch of carbon nanotubes is first mixed with the elastomer, either the same or different from the first elastomer, at a temperature from about 20 to about 200° C. and in the presence of at least one solvent, then the at least one solvent is removed, subsequently and optionally additional elastomers, fillers and additives are added and mixed further to produce a composition suitable for vulcanization.

43. A method of mixing carbon nanotubes and at least one first elastomer, wherein a master batch of carbon nanotubes is first mixed with the elastomer, either the same or different from the first elastomer, at a temperature from about 20 to about 200° C. and in the presence of at least one solvent, subsequently and optionally additional elastomers, fillers and additives are added and mixed further, followed by solvent removal to produce a composition suitable for vulcanization.

The invention claimed is:

1. A dispersion comprising a plurality of oxidized, discrete carbon nanotubes and at least one additive, wherein the oxidized, discrete carbon nanotubes have an aspect ratio of 25 to 500, are multiwall, and are present in the range of greater than zero to about 30% by weight based on the total weight of the dispersion.

2. The dispersion of claim **1** wherein at least 70 percent by weight of the nanotubes are discrete.

3. The dispersion of claim **1** in the form of free flowing particles.

4. The dispersion of claim **1** wherein the oxidized, discrete carbon nanotubes comprise an oxidation species selected from carboxylic acid or a derivative carbonyl containing species wherein the derivative carbonyl species is selected from ketones, quaternary amines, amides, esters, acyl halogens, and monovalent metal salts.

5. The dispersion of claim **1** wherein the oxidized, discrete carbon nanotubes comprise an oxidation species selected from hydroxyl or derived from hydroxyl containing species.

6. The dispersion of claim **1** wherein the oxidized, discrete carbon nanotubes are present in the range of 15% to about 25% by weight based on the total weight of the dispersion.

7. The dispersion of claim **1** wherein the oxidized, discrete carbon nanotubes are present in the range of 18% to about 22% by weight based on the total weight of the dispersion.

8. The dispersion of claim **1**, wherein the additive is selected from the group consisting of dicarboxylic/tricarboxylic esters, timellitates, adipates, sebacates, maleates, glycols and polyethers, polymeric plasticizers, bio-based plasticizers, and mixtures thereof.

9. The dispersion of claim **1**, wherein the additives is a process oil.

10. The dispersion of claim **9**, where in the process oil is selected from the group consisting of naphthenic oils, paraffin oils, paraben oils, aromatic oils, vegetable oils, seed oils, silicones, and mixtures thereof.

11. The dispersion of claim **1**, wherein the additive is a solvent.

12. The dispersion of claim **11**, where in the solvent is selected from the group consisting of substituted or unsubstituted, halogenated or nonhalogenated hydrocarbons.

13. The dispersion of claim **1**, wherein the additive comprises at least one reactive species capable of creating a thermoset polymer.

14. The dispersion of claim **13**, wherein the thermoset polymer is selected from epoxy, polyurethane and silicone.

15. The dispersion of claim **1**, wherein the additive comprises natural wax, synthetic wax, or mixtures thereof.

16. The dispersion of claim **15** further comprising a fluoroelastomer.

17. The dispersion of claim **1** which further comprises at least one filler.

18. The dispersion of claim **17**, wherein the filler has at least one dimension less than about 20 microns.

19. The dispersion of claim **18**, wherein the filler is selected from silicon, lead, lead derivatives, carbon black, graphite, graphene, graphene oxides, paramagnetic particles and mixtures thereof.

20. A dispersion comprising a plurality of oxidized, discrete carbon nanotubes and at least one wax additive and at least one fluoroelastomer, wherein the discrete carbon nanotubes have an aspect ratio of 25 to 500, are multiwall, and are present in the range of greater than zero to about 30% by weight based on the total weight of the dispersion.

21. The dispersion of claim **15** which further comprises a crosslinking agent.

22. The dispersion of claim **15** wherein the additive comprises natural wax wherein the natural wax is plant derived.

23. The dispersion of claim **22** which further comprises a crosslinking agent.

* * * * *

EXHIBIT 3

US010608282B2

(12) **United States Patent**
Bosnyak et al.

(10) **Patent No.: US 10,608,282 B2**
(45) **Date of Patent: Mar. 31, 2020**

(54) **BINDERS, ELECTROLYTES AND SEPARATOR FILMS FOR ENERGY STORAGE AND COLLECTION DEVICES USING DISCRETE CARBON NANOTUBES**

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(65) **Prior Publication Data**

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(Continued)

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(Continued)

(58) **Field of Classification Search**

None

See application file for complete search history.

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(57) **ABSTRACT**

In various embodiments an improved binder composition, electrolyte composition and a separator film composition using discrete carbon nanotubes. Their methods of production and utility for energy storage and collection devices, like batteries, capacitors and photovoltaics, is described. The binder, electrolyte, or separator composition can further comprise polymers. The discrete carbon nanotubes further comprise at least a portion of the tubes being open ended and/or functionalized. The utility of the binder, electrolyte or separator film composition includes improved capacity, power or durability in energy storage and collection devices.

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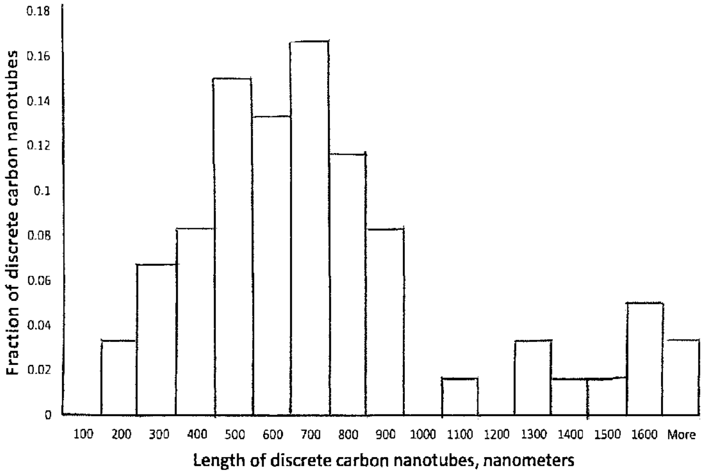

The utility of the electrolyte and or separator film compositions includes improved ion transport in energy storage and collection devices.

16 Claims, 1 Drawing Sheet

Related U.S. Application Data

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H01M 4/14	(2006.01)
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H01G 11/54	(2013.01)
H01G 9/022	(2006.01)
H01G 9/02	(2006.01)
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H01M 4/66	(2006.01)
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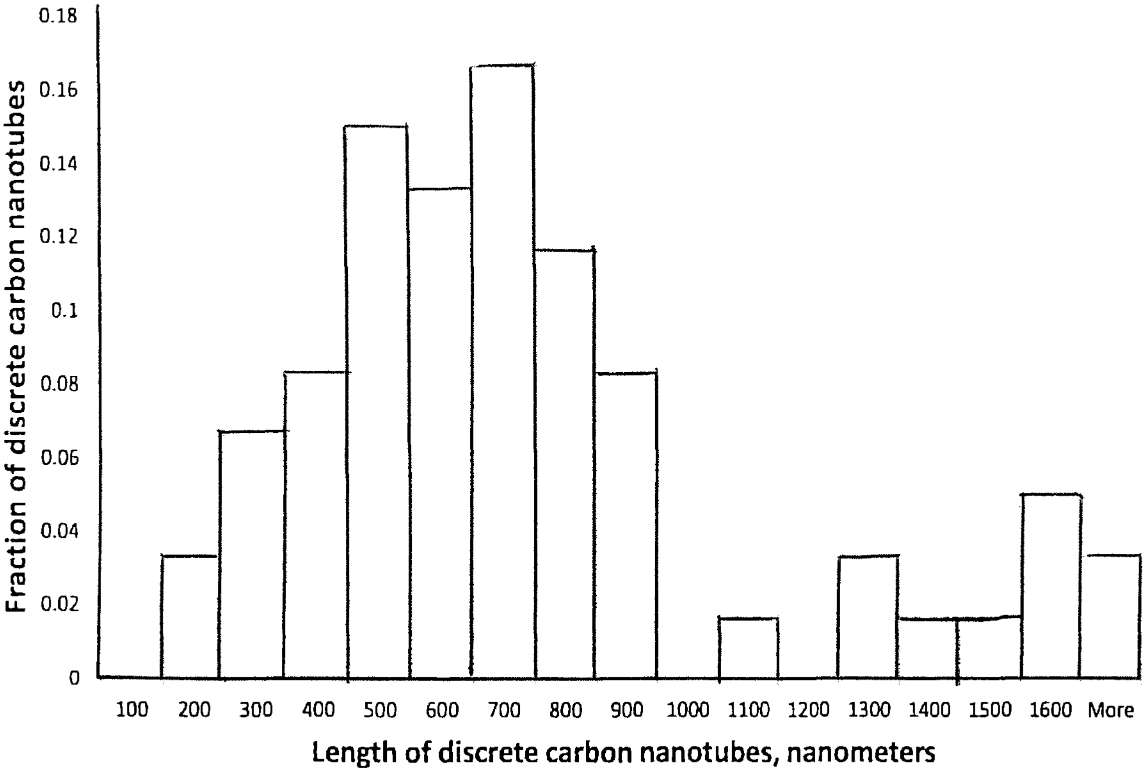
Fraction of discrete carbon nanotubes
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
More
Length of discrete carbon nanotubes, nanometers

BINDERS, ELECTROLYTES AND SEPARATOR FILMS FOR ENERGY STORAGE AND COLLECTION DEVICES USING DISCRETE CARBON NANOTUBES

CROSS REFERENCE TO RELATED APPLICATIONS

This patent application claims priority from U.S. Ser. No. 61/662,393 filed Jun. 21, 2012 and U.S. Ser. No. 61/663,513 filed Jun. 22, 2012; and is related to U.S. Ser. No. 13/164,456 filed Jun. 20, 2011; U.S. Ser. No. 12/968,151 filed Dec. 14, 2010; U.S. Ser. No. 13/140,029 filed Dec. 18, 2009; U.S. Ser. No. 61/500,561 filed Jun. 23, 2011; U.S. Ser. No. 61/500,560 filed Jun. 23, 2011; and U.S. Ser. No. 61/638,454 filed Apr. 25, 2012; the disclosures of which are incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH

Not applicable

BACKGROUND

Many energy storage devices like batteries, capacitors and photovoltaics can utilize a binder and/or an electrolyte and separator film to provide enhanced performances in mechanical stabilization, improved electrical conduction of the powder used in cathodes or electrodes and ion transport in the electro- or photoactive material and electrolyte.

Lithium ion batteries are used extensively for portable electronic equipment and batteries such as lithium ion and lead-acid are increasingly being used to provide electrical back-up for wind and solar energy. The salts for the cathode materials in lithium ion batteries are generally known to have poor electrical conductivity and poor electrochemical stability which results in poor cycling (charge/discharge) ability. Both cathode and anode materials in many battery types such as lithium ion based batteries exhibit swelling and deswelling as the battery is charged and discharged. This spatial movement leads to further separation of some of the particles and increased electrical resistance. The high internal resistance of the batteries, particularly in large arrays of lithium ion batteries such as used in electric vehicles, can result in excessive heat generation leading to runaway chemical reactions and fires due to the organic liquid electrolyte.

Lithium primary batteries consist, for example, of lithium, poly(carbon monofluoride) and lithium tetrafluoroborate together with a solvent such as gamma-butyrolactone as an electrolyte. These lithium primary batteries have excellent storage lifetimes, but suffer from only being able to provide low current and the capacity is about one tenth of what is theoretically possible. This is ascribed to the poor electrical conductivity of the poly(carbon monofluoride). In some cases a portion manganese dioxide is added to aid in the electrical conductivity and power of the lithium battery.

Attempts to overcome the deficiencies of poor adhesion to current collectors and to prevent microcracking during expansion and contraction of rechargable batteries have included development of hinders. Binders such as polyacrylic acid (PAA), for cathodes, poly(styrene butadiene), carboxymethylcellulose (CMC), styrene-butadiene (SBR), for anodes, and particularly polyvinylidene fluoride (PVDF) for cathodes and anodes, are used in lithium based batteries to hold the active material particles together and to maintain contact with the current collectors i.e., the aluminum (Al) or the copper (Cu) foil. The PAA and SBR are used as aqueous suspensions or solutions and are considered more environmentally benign than organic solvent based systems such as n-methyl 2 pyrrolidone (NMP) with PVDF.

A cathode electrode of a lithium ion battery is typically made by mixing active material powder, such as lithium iron phosphate, binder powder, i.e., high molecular weight PVDF, solvent such as NMP if using PVDF, and additives such as carbon black, into a slurry (paste) and pumping this slurry to a coating machine. An anode electrode for a lithium ion battery is made similarly by typically mixing graphite, or other materials such as silicon, as the active material, together with the binder, solvent and additives. The coating machines spread the mixed slurry (paste) on both sides of the Al foil for the cathode and Cu foil for the anode. The coated foil is subsequently calendared to make the electrode thickness more uniform, followed by a slitting operation for proper electrode sizing and drying.

For zinc-carbon batteries, the positive electrode can consist of a wet powder mix of manganese dioxide, a powdered carbon black and electrolyte such as ammonium chloride and water. The carbon black can add electrical conductivity to the manganese dioxide particles, but is needed at high weight percentages in the range about 10 to 50% by weight of manganese dioxide. These high amounts of carbon black needed for improved electrical conductivity, or reduced impedance of the battery, diminish the capacity per unit volume of the battery as less manganese dioxide can be employed per unit volume of the positive paste mix. Thus, in general, there is a need to improve the impedance of a battery while maximizing the amount of active material per unit volume.

For a lead-acid battery the anode can be made from carbon particles together with a binder to provide higher specific capacity (capacity per unit weight). The anode of a zinc-carbon battery is often a carbon rod typically made of compressed carbon particles, graphite and a binder such as pitch. The carbon particle anodes tend to have poor mechanical strength leading to fracture under conditions of vibration and mechanical shock.

The characteristics of the binder material are important for both manufacturing and performance of the battery. Some of these characteristics of relevance are electrical and ionic conductivity, tensile strength and extensibility, adhesion to particles as well as the foils, and swelling of electrolyte. Improvement of electrical and ionic conductivity is needed for improved battery capacity and power. Materials such as lithium manganese oxide for cathodes and silicon particles for anodes exhibit much lower practical specific capacity than theoretically available. A higher electrical and ionic conductivity binder material would be most beneficial to achieve specific capacities closer to their theoretical values. It is desirable to improve the tensile and adhesive strength of binders so that less binder material can be employed and also improve the battery cycling lifetime. Addition of conductive particles, such as carbon black decreases the tensile strength and extensibility of binders. Controlled swelling of the binder in electrolyte is also important. If too much swelling occurs, this separates the particles and significantly increases the inter-particle ohmic resistance. Also, since the particles of the anode or cathode are coated with binder, the layer thickness of the binder can be as thin as 50 to 100 nanometers. This layer thickness precludes uniform distributions of particles of sizes larger than the binder layer thickness. For example, multiwall carbon nanotubes as usually made in a gas phase reactor consist of bundles with diameters ranging from about 50 to 500 microns in diameter and would therefor reside only at the interstitial spaces between the particles.

Impurities, such as non-lithium salts, iron, and manganese to name a few, with the binder can also be highly deleterious to battery performance. Typically, high purity of the binder material, and other additives comprising the binder material such as carbon black to improve electrical conductivity, is an important factor to minimize unwanted side reactions in the electrochemical process. For example in alkaline-manganese dioxide batteries the total iron in the manganese dioxide is less than 100 ppm to prevent hydrogen gassing at the anode. Commercially available carbon nanotubes such as Baytubes® (Bayer AG) or Graphistrength® (Arkema) can contain as much as ten percent or more by weight of residual metal catalysts and are not considered advantageous for batteries at these levels of impurity.

For photovoltaics, lines of conductive paste ink, made from solvents, binders, metal powder and glass frit, are screen-printed onto solar panel modules. The binders are usually polymer based for improved printability, such as ETHOCEL™ (Dow Chemical Company). During the burning off of the polymer and cooling the lines can crack due to shrinkage forces and so increase impedance. It is highly desirable to have a more robust conductive paste ink to prevent cracking during heating and cooling.

Efforts to improve the safety of lithium ion batteries have included using non-flammable liquids such as ionic liquids, for example, ethyl-methyl-imidazolium bis-(trifluoromethanesulfonyl)-imide (EMI-TFSI), and solid polymer, sometimes with additional additives, for example, polyethylene oxide with titanium dioxide nanoparticles, or inorganic solid electrolytes such as a ceramic or glass of the type glass ceramics, $Li_1+x+yTi_2-xAl_xSi_yP_3-yO_{12}$ (LTAP). The electrical conductivity values of organic liquid electrolytes are in the general range of 10^{-2} to 10^{-1} S/cm. Polymer electrolytes have electrical conductivity values in the range of about 10^{-7} to 10^{-4} S/cm, dependent on temperature, whereas inorganic solid electrolytes generally have values in the range 10^{-8} to 10^{-5} S/cm. At room temperature most polymer electrolytes have electrical conductivity values around 10^{-5} S/cm. The low ionic conductivities of polymer and inorganic solid electrolytes are presently a limitation to their general use in energy storage and collection devices. It is thus highly desirable to improve the conductivity of electrolytes, and particularly with polymer and inorganic electrolytes because of their improved flammability characteristics relative to organic liquids. Also, it is desirable to improve the mechanical strength of solid electrolytes in battery applications requiring durability in high vibration or mechanical shock environments, as well as in their ease of device fabrication.

In alkaline batteries the electrolyte is typically potassium hydroxide. Alkaline batteries are known to have significantly poorer capacity on high current discharge than low current discharge. Electrolyte ion transport limitations as well as polarization of the zinc anode are known reasons for this. An increase in the electrolyte ion transport is highly desirable.

Amongst new generation thin film photovoltaic technologies, dye sensitized solar cells (DSSCs) possess one of the most promising potentials in terms of their cost-performance ratio. One of the most serious drawbacks of the present DSSCs technology is the use of liquid and corrosive electrolytes which strongly limit their commercial development. An example of an electrolyte currently used for DSSCs is potassium iodide/iodine. Replacement of the presently used electrolytes is desirable, but candidate electrolytes have poor ion transport.

Typical electrolytic capacitors are made of tantalum, aluminum, or ceramic with electrolyte systems such as boric acid, sulfuric acid or solid electrolytes such as polypyrrole. Improvements desired include higher rates of charge and discharge which is limited by ion transport of the electrolyte.

A separator film is often added in batteries or capacitors with liquid electrolytes to perform the function of electrical insulation between the electrodes yet allowing ion transport. Typically in lithium batteries the separator film is a porous polymer film, the polymer being, for example a polyethylene, polypropylene, or polyvinylidene fluoride. Porosity can be introduced, for example, by using a matt of spun fibers or by solvent and/or film stretching techniques. In lead-acid batteries, where used the separator film is conventionally a glass fiber matt. The polymer separator film comprising discrete carbon nanotubes of this invention can improve ion transport yet still provide the necessary electrical insulation between the electrodes.

The present invention comprises improved binders, electrolytes and separator films for energy storage and collection devices like batteries, capacitors and photovoltaics comprising discrete carbon nanotubes, methods for their production and products obtained therefrom.

SUMMARY

In one embodiment, the invention is a composition comprising a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended, wherein the composition comprises a binder material, an electrolyte material or a separator film of an energy storage or collection device.

In another embodiment, the composition comprises a plurality of discrete carbon nanotube fibers have a portion of discrete carbon nanotubes that are open ended and ion conducting. The composition can further comprise at least one polymer. The polymer is selected from the group consisting of vinyl polymers, preferably poly(styrene-butadiene), partially or fully hydrogenated poly(styrene butadiene) containing copolymers, functionalized poly(styrene butadiene) copolymers such as carboxylated poly(styrene butadiene) and the like, poly(styrene-isoprene), poly(methacrylic acid), poly(acrylic acid), poly(vinylalcohols), and poly(vinylacetates), fluorinated polymers, preferably poly (vinylidine difluoride) and poly(vinylidene difluoride) copolymers, conductive polymers, preferably poly(acetylene), poly(phenylene), poly(pyrrole), and poly(acrylonitrile), polymers derived from natural sources, preferably alginates, polysaccharides, lignosulfonates, and cellulosic based materials, polyethers, polyolefines, polyesters, polyurethanes, and polyamides; homopolymers, graft, block or random co- or ter-polymers, and mixtures thereof.

In yet another embodiment of this invention, the plurality of discrete carbon nanotube fibers are further functionalized, preferably the functional group comprises a molecule of mass greater than 50 g/mole, and more preferably the functional group comprises carboxylate, hydroxyl, ester, ether, or amide moieties, or mixtures thereof.

A further embodiment of this invention comprising a plurality of discrete carbon nanotube fibers further comprising at least one dispersion aid.

In a yet further embodiment of this invention, the plurality of carbon nanotubes further comprise additional inorganic structures comprising of elements of the groups two through fourteen of the Periodic Table of Elements.

Another embodiment of this invention comprises a plurality of carbon wherein the composition has a flexural strength of at least about ten percent higher than a comparative composition made without the plurality of discrete carbon nanotubes.

Yet another embodiment of this invention is a binder, electrolyte or separator film composition comprising a plurality of discrete carbon nanotube fibers having a portion of discrete carbon nanotubes that are open ended and ion conducting further comprising non-fiber carbon structures. The non-fiber carbon structures comprise components selected from the group consisting of carbon black, graphite, graphene, oxidized graphene, fullerenes and mixtures thereof. Preferably the graphene or oxidized graphene have at least a portion of discrete carbon nanotubes interspersed between the graphene or oxidized graphene platelets.

A yet further embodiment of this invention is a composition comprising a plurality of discrete carbon nanotube fibers where the binder material has an impedance of less than or equal to about one billion (1×10^9) ohm-m and the electrolyte material has a charge transfer resistance of less than or equal to about 10 million (1×10^7) ohm-m.

Another embodiment of this invention comprises an electrolyte or separator film composition comprising a plurality of discrete carbon nanotube fibers wherein the carbon nanotubes are oriented. The orientation is accomplished by fabrication techniques such as in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or fiber spinning fabrication method. The orientation may also be made via post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.

A further embodiment of this invention is a composition comprising a plurality of discrete carbon nanotubes wherein the portion of open ended tubes comprise electrolyte. For an electrolyte comprising polymer, the polymer is preferred to comprise a molecular weight of the polymer less than 10,000 daltons, such that the polymer can enter within the tube. The electrolyte may contain liquids.

An additional embodiment of this invention comprises a composition including a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended, preferably wherein 40% to 90% by number of the carbon nanotubes have an aspect ratio of 30-70, and more preferably aspect ratio of 40-60, and 1% to 30% by number of aspect ratio 80-140, most preferably an aspect ratio of 90 to 120. In statistics, a bimodal distribution is a continuous probability distribution with two different modes. These appear as distinct peaks (local maxima) in the probability density function. More generally, a multimodal distribution is a continuous probability distribution with two or more modes. The discrete carbon nanotubes can have a unimodal, bimodal or multimodal distribution of diameters and/or lengths. For example, the discrete carbon nanotubes can have a bimodal distribution of diameters wherein one of the peak values of diameter is in the range 2 to 7 nanometers and the other peak value is in the range 10 to 40 nanometers. Likewise, the lengths of the discrete carbon nanotubes can have a bimodal distribution such that one peak has a maximum value in the range of 150 to 800 nanometers and the second peak has a maximum value in the range 1000 to 3000 nanometers, That composition is useful in binders and electrolytes of the invention.

In yet another embodiment, the invention is an electrode paste, preferably an anode paste, for a lead acid battery, the paste comprising discrete carbon nanotubes having an average length from about 400 to about 1400 nm, polyvinyl alcohol, water, lead oxide and sulfuric acid. Preferably, the carbon nanotubes, polyvinyl alcohol and water form a dispersion, and the dispersion is then contacted with lead oxide followed by sulfuric acid to form the electrode paste.

BRIEF DESCRIPTION OF FIGURES

The following drawings form part of the present specification and are included to further demonstrate certain aspects of the present invention. The invention may be better understood by reference to one or more of these drawings in combination with the detailed description of specific embodiments presented herein.

FIG. **1** shows discrete carbon nanotubes of this invention with a bimodal length distribution where the maximum of one peak is about 700 nanometers and the maximum of the second peak is about 1600 nanometers. The lengths were determined by deposition of the discrete carbon nanotubes on a silicon wafer and by using scanning electron microscopy.

DETAILED DESCRIPTION

In the following description, certain details are set forth such as specific quantities, sizes, etc., so as to provide a thorough understanding of the present embodiments disclosed herein. However, it will be evident to those of ordinary skill in the art that the present disclosure may be practiced without such specific details. In many cases, details concerning such considerations and the like have been omitted inasmuch as such details are not necessary to obtain a complete understanding of the present disclosure and are within the skills of persons of ordinary skill in the relevant art.

While most of the terms used herein will be recognizable to those of ordinary skill in the art, it should be understood, that when not explicitly defined, terms should be interpreted as adopting a meaning presently accepted by those of ordinary skill in the art. In cases where the construction of a term would render it meaningless or essentially meaningless, the definition should be taken from Webster's Dictionary, 3rd Edition, 2009. Definitions and/or interpretations should not be incorporated from other patent applications, patents, or publications, related or not, unless specifically stated in this specification.

In the present invention, discrete oxidized carbon nanotubes, alternatively termed exfoliated carbon nanotubes, are obtained from as-made bundled carbon nanotubes by methods such as oxidation using a combination of concentrated sulfuric and nitric acids and sonication. The bundled carbon nanotubes can be made from any known means such as, for example, chemical vapor deposition, laser ablation, and high pressure carbon monoxide synthesis. The bundled carbon nanotubes can be present in a variety of forms including, for example, soot, powder, fibers, and bucky paper. Furthermore, the bundled carbon nanotubes may be of any length, diameter, or chirality. Carbon nanotubes may be metallic, semi-metallic, semi-conducting, or non-metallic based on their chirality and number of walls. They may also include amounts of nitrogen within the carbon wall structure. The discrete oxidized carbon nanotubes may include, for example, single-wall, double-wall carbon nanotubes, or multi-wall carbon nanotubes and combinations thereof. The diameters and lengths of the discrete carbon nanotubes can be determined by deposition of the discrete carbon nanotubes from dilute solution on a silicon wafer and by using scanning electron microscopy.

One of ordinary skill in the art will recognize that many of the specific aspects of this invention illustrated utilizing a particular type of carbon nanotube may be practiced equivalently within the spirit and scope of the disclosure utilizing other types of carbon nanotubes.

Functionalized carbon nanotubes of the present disclosure generally refer to the chemical modification of any of the carbon nanotube types described hereinabove. Such modifications can involve the nanotube ends, sidewalls, or both. Chemical modifications may include, but are not limited to covalent bonding, ionic bonding, chemisorption, intercalation, surfactant interactions, polymer wrapping, cutting, solvation, and combinations thereof.

Any of the aspects disclosed in this invention with discrete carbon nanotubes may also be modified within the spirit and scope of the disclosure to substitute other tubular nanostructures, including, for example, inorganic or mineral nanotubes. Inorganic or mineral nanotubes include, for example, silicon nanotubes, boron nitride nanotubes and carbon nanotubes having heteroatom substitution in the nanotube structure, such as nitrogen. The nanotubes may include or be associated with organic or inorganic elements or compounds from elements such as, for example, carbon, silicon, boron and nitrogen. The inorganic elements can comprise of elements of the groups two through fourteen of the Periodic Table of Elements, singly or in combination. Association may be on the interior or exterior of the inorganic or mineral nanotubes via Van der Waals, ionic or covalent bonding to the nanotube surfaces.

Dispersing agents to aid in the dispersion of discrete carbon nanotubes or other components of this invention are, for example, anionic, cationic or non-ionic surfactants, such as sodium dodecylsulfonate, cetyltrimethyl bromide or polyethers such as the Pluronic made by BASF. They can be physically or chemically attached to the discrete carbon nanotubes. In some cases the dispersing aid can also act as a binder. For example, with lead-acid batteries polyvinylalcohol can be used to disperse discrete carbon nanotubes of this invention in water among the paste particles then on addition of sulfuric acid the polyvinylalcohol is considered to deposit on the paste particle and act as a binder. The polyvinylalcohol is preferred to have an average molecular weight less than about 100,000 daltons.

In some embodiments, the present invention comprises a composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising a plurality of discrete carbon nanotube fibers The nanotube fibers may have an aspect ratio of from about 10 to about 500, and at least a portion of the discrete carbon nanotube fibers may be open ended. The portion of discrete carbon nanotubes that are open ended may be conducting.

In some embodiments of the present invention, the composition may further comprise at least one polymer. The polymer may be selected from the group consisting of vinyl polymers, such as poly(styrene-butadiene), partially or fully hydrogenated poly(styrene butadiene) containing copolymers, functionalized poly(styrene butadiene) copolymers such as carboxylated poly(styrene butadiene), poly(styrene-isoprene), poly(methacrylic acid), poly(methylmethacrylate), poly(acrylic acid), poly(vinylalcohols), poly(vinylacetates), fluorinated polymers, polyvinylpyrrolidone, conductive polymers, polymers derived from natural sources, polyethers, polyesters, polyurethanes, and polyamides; homopolymers, graft, block or random co- or terpolymers, and mixtures thereof.

In further embodiments, the composition of the present invention may comprise carbon nanotubes which are further functionalized. The composition of the present invention may comprise additional inorganic structures comprising elements of the groups two through fourteen of the Periodic Table of Elements. The composition of the present invention may further comprise at least one dispersion aid.

The composition of the present invention may further comprise an alcohol, such as polyvinyl alcohol.

In some embodiments, the present invention comprises a binder material further comprise non-fiber carbon structures, for example carbon black, graphite, graphene, oxidized graphene, fullerenes, and mixtures thereof. In some embodiments, at least a portion of discrete carbon nanotubes are interspersed between graphene and/or oxidized graphene plates. In this embodiment, the binder material may have an impedance of less than or equal to about one billion ohm-m.

In further embodiments, the composition of the present invention comprises an electrolyte material or separator film. The composition may have a charge transfer resistance of less than or equal to about 10 million ohm-m.

In further embodiments, the carbon nanotubes of the present invention are oriented, for example in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or fiber spinning fabrication method. Orientation may be accomplished using post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.

In some embodiments of the present invention, a portion of open ended tubes comprise electrolyte. The electrolyte may comprise a polymer or a liquid.

In further embodiments of the invention, 40% to 90% by number of the discrete carbon nanotubes have an aspect ratio of 30-70. In other embodiments, 1% to 30% by number of carbon nanotubes have an average aspect ratio 80-140.

In some embodiments, the present invention comprises an electrode paste for a lead-acid battery comprising discrete carbon nanotubes having an average length from about 400 to about 1400 nm. The electrode paste may further comprise an alcohol, for example polyvinyl alcohol.

The present invention also comprises a method for making a composition for use as a binder material, an electrolyte material or a separator film material for an energy storage or collection device. The method comprises the steps of a) adding carbon nanotubes to a liquid, solvent or polymer melt b) vigorous mixing such as with a sonicator or high shear mixer for a period of time; and c) optionally adding further materials, such as PVDF, and inorganic fillers such as carbon black and continued mixing until a homogenous dispersion is obtained. The mixture can then be further fabricated into shapes by such methods as film extrusion, fiber extrusion, solvent casting, and thermoforming. The method may further comprise adding a polymer, a dispersion aid, additional inorganic structures, or an alcohol, such a polyvinyl alcohol.

Electrolytes

The term electrolyte is defined as a solution able to carry an electric current. An ionic salt is dissolved in a medium which allows ion transport. Ion transport is defined as the movement of ions through the electrolyte. The ions are preferably a single type of ion, but can be a mixture of types of ions. The medium can be solid, liquid or semi-solid, for example gelatinous. For example, in a lead-acid battery the electrolyte medium is preferred to be liquid or gelatinous. For a lithium based battery the electrolyte medium is preferred to be gelatinous and more preferably a solid at use temperature to prevent high concentrations of flammable organic liquids which could escape on battery failure by shorting or penetration. The electrolyte has to be sufficiently non-electrically conductive to prevent poor storage stability or shorting.

A separator film is often added in batteries with liquid electrolytes to perform the function of electrical insulation between the electrodes yet allowing ion transport. Typically in lithium batteries the separator film is a porous polymer film, the polymer being, for example a polyethylene, polypropylene, or polyvinylidene fluoride. Porosity can be introduced, for example, by using a matt of spun fibers or by solvent and/or film stretching techniques. In lead-acid batteries, where used the separator film is conventionally a glass fiber matt. The separator film comprising discrete carbon nanotubes of this invention can improve ion transport yet still provide the necessary electrical resistivity. The degree of electrical conductivity can be controlled by the amount of discrete carbon nanotubes within the binder or separator film medium. In a binder it may be advantageous to use higher levels of discrete carbon nanotubes, for example in the range 10 to 50% by weight of the binder medium, for the optimum balance of low electrical resistivity, for example, less than 1×10^7 ohm-m, with strength, than for the electrolyte medium or separator film where it may be advantageous to use less than 10% weight of discrete carbon nanotubes to maintain electrical resistivity greater than about 1×10^7 ohm-m. The use of discrete carbon nanotubes to improve the strength and ease of battery assembly of the thin electrolyte or separator films is also considered valuable.

The flexural strength or resistance to cracking of the solid electrolytes can be determined by flexural bending of a film or sheet of the solid electrolyte on a thin aluminum or copper film in a 3-point bending fixture and an Instron Tensile Testing machine. The test is analogous to standard test procedures given in ASTM D-790. The resistance to deformation and stress to crack the solid electrolyte through the solid electrolyte film thickness is recorded. Units are in MPa.

Ionic salts can be added to a polymeric medium such as polyethylene oxide to produce electrolytes. For example, for lithium ion batteries ionic salts, such as lithium perchlorate, lithium tetrafluoroborate, lithium trifluoromethanesulfate, lithium bistrifluoromethanesulfonimide, lithium bisoxalatoborate can be added to the polymer, by solvent or to the polymer melt. Solvents can be those that are retained as an electrolyte medium, for example, ethylene carbonate, propylene carbonate, or solvents which are then removed by drying such as acetonitrile.

The electrolyte or separator film containing polymeric material may have a polymer, or a combination of polymers that are dissimilar by molecular weight and or by type. For example, in an electrolyte containing polyethylene oxide a portion of the polyethylene oxide can be of molecular weight above about 200,000 daltons and a portion less than about 10,000 daltons. As another example, the polyethylene oxide can be partially replaced by another polymer, such as polyvinylidene fluoride, polyvinylpyrrolidone, or polymethylmethacrylate.

Procedure for Impedance and Swelling Evaluation of Binder Materials

Each dried sample film is obtained using a 22 mm diameter punch. Films are also obtained saturated with neat electrolyte (a 50/50 composition of ethylene carbonate and propylene carbonate) and electrolyte and 50% by weight of lithium perchlorate by immersing the films for 1-20 days at room temperature. The films are evaluated for swelling by weight increase and tested for impedance using an LCR meter, (Agilent 4263B) at 25 degrees centigrade and under about 70 psi, (0.483 MPa) pressure at 1 Khz. The units of impedance are usually given as ohm-meter.

The flexural strength or resistance to cracking of the pastes can be determined by flexural bending of the paste on a thin aluminum or copper film in a 3-point bending fixture and an Instron Tensile Testing machine. The test is analogous to standard test procedures given in ASTM D-790. The stress to crack the paste through the paste thickness is recorded. Units are in MPa.

The adhesive strength of the pastes can be determined by using lap shear strength procedures and the Instron Tensile Testing Machine. The test is analogous to EN 1465. The specimen consists of two rigid substrates, for example aluminum sheets or copper sheets, bonded together by the paste in a lapped joint. This causes the two ends of the specimen to be offset from the vertical load line of the test. The paste is placed between two strip of material. The stress to failure on pulling the lapped specimen is recorded. Units are in MPa.

Procedure for Charge Transfer Resistance Evaluation of Electrolyte Materials

Electrolyte films are placed between two electrodes the resistance and reactance determined at frequencies of 100 Hz, 120 Hz, 1 KHz, 10 KHz and 100 KHz using an LCR meter, (Agilent 4263B) at 25 degrees centigrade and a 2 volt dc bias with a sinusoidal test level of 20 mv. A Nyquist plot is contructed of the real and imaginary components of the impedance from which the charge transfer resistance is obtained.

EXAMPLES 1-3

Compositions Consisting of Discrete Carbon Nanotubes in Poly(Vinylidene Fluoride) for Binders and Separator Films

General procedure. A dispersion of discrete carbon nanotubes in n-methyl-2-pyrrolidone (NMP) is first made by adding carbon nanotubes of about 2% weight of oxidized moieties and average aspect ratio about 60 to NMP under vigorous stirring. Following addition, sonication is applied for about 15 minutes to exfoliate the carbon nanotubes. An amount of PVDF is slowly added to the system over a period of 30 minutes to obtain the desired weight fraction of carbon nanotube to PVDF. Vigorous stirring and sonication is continued until a homogenous dispersion was obtained. A uniform black colored film of PVDF is obtained by removing the NMP in vacuo to constant weight.

Examples 1-3 are dried PVDF films containing discrete carbon nanotubes in the weight percentage 2.5, 7.5 and 10%, respectively, and are shown in Table 1.

Control 1 is made in a similar manner as Example 1 except that no discrete carbon nanotubes are added. The resultant dried film is a pale yellow. The impedance measurements of the dry films and films swollen for 20 days in a mixture of ethylene carbonate and propylene carbonate 50/50 and 50% by weight of lithium perchlorate are provided in Table 1.

The results shown in Table 1 demonstrate that Examples 1-3 with discrete oxidized carbon nanotubes of this invention in PVDF gave significantly lower values of impedance than the control 1 of PVDF film alone. Furthermore, inclusion of carbon nanotubes of this invention in PVDF demonstrate higher mass uptake of the $LiClO_4$ solvent mixture which enables improved ion transport. These improved properties on addition of discrete carbon nanotubes of this invention should lead to much enhanced performance as a binder or separator film.

TABLE 1

PVDF	% wt Carbon nanotubes	% mass uptake in ECO/PCO and $LiClO_4$	Volume resistivity Dry Ohm-m	Volume resistivity swollen with ECO/PCO & $LiClO_4$, ohm-m
Control 1	0	6	1.579×10^{12}	3.035×10^{11}
Example 1	2.5	7	1.315×10^{11}	1.403×10^{10}
Example 2	7.5	9	3.326×10^{7}	1.239×10^{9}
Example 3	10	14	1.216×10^{8}	3.694×10^{8}

EXAMPLES 4 AND 5

Binder Composition of Discrete Carbon Nanotubes (w/w) in SBR Latex

A polyether (BASF, Pluronic F-127) as a dispersing aid for the discrete carbon nanotubes is dissolved in water cleaned by reverse osmosis at a weight ratio of 1.5 to 1 of the polyether to dry oxidized carbon nanotubes, then oxidized carbon nanotubes are added at a concentration of 1.5 weight/volume carbon nanotubes to water and sonicated for a period of 30 minutes to disperse the oxidized carbon nanotubes. SBR latex (Dow Chemical Company, grade CP 615 NA, 50% solids content) is added directly to the exfoliated carbon nanotubes at the desired carbon nanotube to SBR weight ratio and stirred vigorously until homogenous. A black film is obtained on drying the mixture in air, followed by drying in vacuo until constant weight of the film is obtained.

Example 4 is made with five weight percent of discrete carbon nanotubes to dry SBR.

Example 5 is made with seven point five weight percent of discrete carbon nanotubes to dry SBR.

Control 2 is made as example 4 and 5 except no discrete carbon nanotubes are added. The film is clear.

The impedance measurements of the dry films and films swollen for 2 days in a mixture of ethylene carbonate, ECO, and propylene carbonate, PCO, 50/50 and 50% by weight of lithium perchlorate are provided in table 2. The results demonstrate inclusion of discrete carbon nanotubes of this invention with SBR provide a significant reduction in impedance.

TABLE 2

SBR	% weight carbon nanotubes	% mass uptake* ECO/PCO $LiClO_4$	Volume resistivity Ohm-m
Control 2	0	−3	9.99×10^{11}
Example 4	5	−2	4.241×10^{11}
Example 5	7.5	−2	1.073×10^{11}

*2 day swell

EXAMPLE 6

Formation of a Solid Electrolyte Contained Discrete Carbon Nanotubes wherein the Tubes are Further Functionalized with Polyethylene Oxide

Oxidized carbon nanotube fibers are made by first sonicating the carbon nanotube fiber bundles (CNano, grade 9000) at 1% w/v in a mixture of concentrated sulfuric acid/nitric acid for 2 hours or more at about 30° C. After filtering and washing with water the pH of the final washing is about 4. The oxidized carbon nanotube fibers are dried in vacuo for 4 hours at about 80° C. The resultant oxidized tubes generally contain about 1.5-6% by weight of oxygenated species as determined by thermogravimetric analysis in nitrogen between 200 and 600° C. and at least a portion of the tubes are open ended as determined by secondary electron microscopy. The residual ash after burning the oxidized carbon nanotubes in air to 800° C. is about 0.5 to 2% w/w. Monohydroxy poly(ethylene glycol), PEG-MH, of molecular weight about 1900 daltons (Sigma Aldridge) is added in excess to the dried oxidized nanotubes together with a small amount of sulfuric acid as a catalyst and the mixture heated to 100° C. while sonicating for about 1 hour. After cooling and addition of water the functionalized carbon nanotubes are filtered followed by washings to remove excess PEG-MH and sulfuric acid. The functionalized carbon nanotubes are dried in vacuo at 40° C. overnight. 0.5% w/w of the carbon nanotubes reacted with PEG-MH are added to PEG-MH, heated to 60° C. and sonicated for 30 minutes. A uniform black liquid is obtained which on examination while in the liquid state by optical microscopy up to 150× magnification revealed no discernible aggregates of carbon nanotubes, i.e. the tubes are discrete and dispersed On cooling, the PEG-MH with discrete carbon nanotubes the PEG-MH is observed to crystallize and carbon nanotubes are observed to be between crystal lamellae, i.e., in the amorphous regions of the solid polymer. This is considered very advantageous as ions are recognized to travel preferentially in the amorphous regions.

EXAMPLES 7-15

Solid Electrolyte Compositions with Discrete Carbon Nanotubes

Discrete carbon nanotubes of oxidation about 2% and an average aspect ratio of 60, with a portion of the carbon nanotubes being open-ended are dried in vacuo at 80° C. for four hours. Compositions are made up as detailed in table 3 by first making solutions of the components using acetonitrile (Sigma Aldridge, 99.8% anhydrous) as a solvent; a 1% w/v solution of the discrete carbon nanotubes, a 2.5% w/v of polyethylene oxide, PEO, (Alfa Aesar) consisting of a ratio of two PEO's, one of molecular weight 300,000 daltons and the other molecular weight 4000 daltons in the weight ratio 1:0.23, respectively, and 5% w/v solution of lithium trifluoromethanesulfate (Aldrich). The dried discrete carbon nanotubes are first sonicated in acetonitrile for 30 minutes using a sonicator bath. The solutions are made to the various compositions (parts per hundred of PEO) given in Table 3, then sonicated for 30 minutes at around 30° C. in a sonicator bath (Ultrasonics). The mixtures are then transferred to a glass dish and the acetonitrile evaporated for 4 hours to give films. The films are dried in vacuo at 50° C. for 2 hours followed by compression molded at 120° C. for 3 minutes and 20 tons platen pressure between polyethylene terephthalate sheets, cooled to room temperature and stored in a dessicator before testing.

The results in Table 3 show that significant improvements are gained in the conductivity of the solid electrolyte films with addition of discrete carbon nanotubes of this invention compared to the controls. The electrolyte films made with discrete carbon nanotubes are also seen to have higher strength than the controls as judged by their ability to be handled without tearing.

TABLE 3

	$LiCF_3SO_3$ phr	PEO phr	Discrete Carbon nanotubes phr	Conductivity at 10 KHz, 25° C., S/cm
Control 3	15	100	0.0	3.89×10^{-5}
Control 4	20	100	0.0	1.49×10^{-5}
Control 5	30	100	0.0	4.90×10^{-6}
Example 7	15	100	1.5	6.21×10^{-4}
Example 8	20	100	1.5	5.74×10^{-4}
Example 9	30	100	1.5	4.32×10^{-4}
Example 10	15	100	2.0	1.27×10^{-4}
Example 11	20	100	2.0	2.27×10^{-4}
Example 12	30	100	2.0	2.67×10^{-4}
Example 13	15	100	3.0	3.62×10^{-4}
Example 14	20	100	3.0	1.11×10^{-4}
Example 15	30	100	3.0	2.89×10^{-4}

EXAMPLE 16

Paste Composition Containing Discrete Carbon Nanotubes for Lead-Acid Battery

The compositions for making an anode paste for a lead acid battery for control 6 and example 16 is shown in Table 4. The expander (Hammond) is a composition of lignin sulfonate, barium sulfate and carbon black in the weight ratio 1:1:0.5, respectively. The expander is added to the dry powder of lead oxide, then water is added and mixed, followed by slow addition and mixing of acid (sulfuric acid, 1.4 specific gravity) while maintaining the temperature below 55° C. In example 16, discrete carbon nanotubes of average length 700 nanometers and oxidation level about 2% and polyvinyl alcohol, PVA, (Sigma Aldridge, average molecular weight 30,000 to 70,000 daltons, 87 to 90% hydrolyzed) are admixed with water and sonicated to give a dispersion of discrete carbon nanotubes of 2.25% by weight and PVA of 3.375% by weight. The discrete carbon nanotube solution is added together with the water to the lead oxide followed by slow addition of the sulfuric acid. The anode material is pasted to a lead grid and assembled into a battery with a lead oxide cathode, followed by standard battery formation as recorded elsewhere, i.e., Lead-Acid Batteries: Science and Technology: Science and Technology, Elsevier 2011. Author: D. Pavlov. The weight % of discrete carbon nanotubes to dry lead oxide in the anode paste is 0.16.

Relative to Control 6, Example 16 showed a higher charge efficiency of at least 30% at 14.2 v charging voltage, an increase rate of charge of at least 200% and at least 50% lower polarization between 14 and 15 volts. Polarization is the difference between the voltage of the battery under equilibrium and that with a current flow.

TABLE 4

	Control 6 Kg	Example 16 Kg
Lead Oxide	230	230
Fiber flock	0.15	0.15
Expander	1.4	1.4
Discrete carbon nanotubes	0	0.368
Polyvinylalcohol	0	0.552
Water	27	27
Sulfuric acid 1.4 sg	23.1	23.1

What is claimed is the following:

1. A composition for use as a binder material, an electrolyte material or a separator film material of an energy storage or collection device, comprising:

a plurality of discrete carbon nanotube fibers, said fibers having an aspect ratio of from about 10 to about 500, and wherein at least a portion of the discrete carbon nanotube fibers are open ended and

wherein 40% to 90% by number of the discrete carbon nanotubes have an aspect ratio of 30-70 and wherein from 1% to 30% by number of discrete carbon nanotubes have an average aspect ratio 80-140.

2. The composition of claim **1**, wherein the portion of discrete carbon nanotubes that are open ended are ion conducting.

3. The composition of claim **2**, further comprising additional inorganic structures comprising elements of the groups two through fourteen of the Periodic Table of Elements.

4. The composition of claim **2**, further comprising non-fiber carbon structures selected from the group consisting of carbon black, graphite, graphene, oxidized graphene, fullerenes, and mixtures thereof.

5. The composition of claim **1**, further comprising at least one polymer.

6. The composition of claim **5**, wherein the polymer is selected from the group consisting of vinyl polymers, poly (styrene-butadiene), partially or fully hydrogenated poly (styrene butadiene) containing copolymers, functionalized poly(styrene butadiene) copolymers such as carboxylated poly(styrene butadiene), poly(styrene-isoprene), poly(methacrylic acid), poly(methylmethacrylate), poly(acrylic acid), poly(vinylalcohols), poly(vinylacetates), fluorinated polymers, polyvinylpyrrolidone, conductive polymers, polymers derived from natural sources, polyethers, polyesters, polyurethanes, and polyamides; homopolymers, graft, block or random co- or ter-polymers, and mixtures thereof.

7. The composition of claim **1**, wherein the carbon nanotubes are further functionalized.

8. The composition of claim **1**, further comprising at least one dispersion aid.

9. The composition of claim **1**, further comprising at least a portion of discrete carbon nanotubes interspersed between graphene and/or oxidized graphene plates.

10. The composition of claim **1**, wherein the binder material has an impedance of less than or equal to about one billion ohm-m.

11. The composition of claim **1**, where the electrolyte material or separator film has a charge transfer resistance of less than or equal to about 10 million ohm-m.

12. The composition of claim **1**, wherein the carbon nanotubes are oriented.

13. The composition of claim **12**, wherein the orientation is accomplished in a sheet, micro-layer, micro-layer with vertical film orientation, film, molding, extrusion, or fiber spinning fabrication method.

14. The composition of claim **12**, wherein orientation includes post fabrication methods, such as tentering, uniaxial orientation, biaxial orientation and thermoforming.

15. The composition of claim **1**, which further comprises electrolyte.

16. The composition of claim **15**, wherein the electrolyte comprises a polymer or a liquid.

* * * * *

EXHIBIT 4

PRODUCT SPECIFICATION

Rechargeable Lithium Ion Battery
Model : INR18650HG2 3000mAh

LG Twin Towers 128, Yeoui-daero, Yeongdeungpo-gu,
Seoul, Republic of Korea, 150-721

http://www.lgchem.com

Revision History

Revision	Date	Originator	Description
0	2014-04-24	Shin Chorong	- Original Release

Contents

1. General Information

1.1 Scope

This product specification defines the requirements of the rechargeable lithium ion battery to be supplied to the customer by LG Chem.

1.2 Application: Power Tools

1.3 Product classification: Cylindrical rechargeable lithium ion battery

1.4 Model name: 18650 HG2

2. Nominal Specification

Item	Condition / Note	Specification
2.1 Capacity	Std. charge / discharge	Nominal 3000 mAh (C_{nom})
2.2 Nominal Voltage	Average for Std. discharge	3.60V
2.3.1 Standard Charge (Refer to 4.1.1)	Constant current Constant voltage End condition(Cut off)	1500mA 4.2V 50mA
2.3.2 Fast charge (Refer to 4.1.3)	Constant current Constant voltage End condition(Cut off)	4000mA 4.2V 100mA
2.4 Max. Charge Voltage	-	4.20±0.05V
2.5 Max. Charge Current	-	4000mA
2.6.1 Standard Discharge (Refer to 4.1.2)	Constant current End voltage(Cut off)	600mA 2.5V
2.6.2 Fast Discharge (Refer to 4.1.3)	Constant current End voltage(Cut off)	10000mA , 20000mA 2.5V
2.7 Max. Discharge Current	For continuous discharge	20000mA
2.8 Weight	Max.	47.0 g
2.9 Operating Temperature (Cell Surface Temperature)	Charge Discharge	0 ~ 50℃ -20 ~ 75℃
2.10 Storage Temperature (for shipping state[i])	1 month 3 month 1 year	-20 ~ 60℃ -20 ~ 45℃ -20 ~ 20℃

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* Shipping state : About 40% capacity of fully charged state

3. Appearance and Dimension

3.1 Appearance

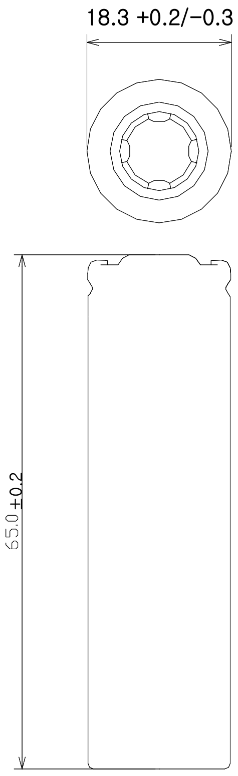
There shall be no such defects as deep scratch, crack, rust, discoloration or leakage, which may affect the commercial value of the cell.

3.2 Dimension

Diameter : 18.3 + 0.2/-0.3 mm (Max. 18.5 mm)

Diameter is defined as the largest data value measured on the “A” area of a cylindrical cell.

Height : 65.0 ± 0.2 mm (Max. 65.2 mm)



4. Performance Specification

4.1 Standard test condition

4.1.1 Standard Charge

Unless otherwise specified, “Standard Charge” shall consist of charging at constant current of 1500mA. The cell shall then be charged at constant voltage of 4.2V while tapering the charge current. Charging shall be terminated when the charging current has tapered to 50mA. For test purposes, charging shall be performed at 23ºC ± 2ºC.

4.1.2 Standard Discharge

"Standard Discharge" shall consist of discharging at a constant current of 600mA to 2.5V. Discharging is to be performed at 23 ºC ± 2 ºC unless otherwise noted (such as capacity versus temperature).

4.1.3 Fast Charge / Discharge condition

Cells shall be charged at constant current of 4000mA to 4.2V with end current of 100mA. Cells shall be discharged at constant current of 10000mA and 20000mA to 2.5V. Cells are to rest 10 minutes after charge and 30 minutes after discharge.

4.2 Electrical Specification

Item	Condition	Specification
4.2.1 Initial AC Impedance	Cell shall be measured at 1kHz after charge per 4.1.1.	≤ 20 mΩ, without PTC
4.2.2 Initial Capacity	Cell shall be charged per 4.1.1 and discharged per 4.1.2 within 1h after full charge.	3000 mAh (C_{nom})
4.2.3 Cycle Life	Cells shall be charged and discharged per 4.1.3, 300 cycles(10A) and 200 cycles(20A) .A cycle is defined as one charge and one discharge. 301st (10A) and 201st (20A) discharge capacity shall be measured per 4.1.1 and 4.1.2	≥ 70 % (of C_{nom} in 2.1)

4.3 Environmental specification.

Item	Condition	Specification
4.3.1 Storage Characteristics	Cells shall be charged per 4.1.1 and stored in a temperature-controlled environment at 23ºC ± 2ºC for 30 days. After storage, cells shall be discharged per 4.1.2 to obtain the remaining capacity[*].	Capacity remaining rate ≥ 90% (of C_{nom} in 2.1)
4.3.2 High Temperature Storage Test	Cells shall be charged per 4.1.1 and stored in a temperature-controlled environment at 60ºC for 1 week. After storage, cells shall be discharged per 4.1.2 and cycled per 4.1.1 and 4.1.2 for 3 cycles to obtain recovered capacity[*].	No leakage, Capacity recovery rate ≥ 80% (of C_{nom} in 2.1)

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* Remaining Capacity : After storage, cells shall be discharged with standard condition(4.1.2) to measure the remaining capacity.

** Recovery Capacity : After storage, cells shall be discharged with standard discharge condition(4.1.2), and then cells shall be charged with standard charge condition(4.1.1), and then discharged with standard discharge condition(4.1.2). This charge / discharge cycle shall be repeated three times to measure the recovery capacity.

<table>
<tr><td>4.3.3
Thermal Shock Test</td><td colspan="2">65ºC (8h) ← 3hrs → -20ºC (8h) for 8 cycles with cells charged per 4.1.1 After test, cells are discharged per 4.1.2 and cycled per 4.1.1 and 4.1.2 for 3 cycles to obtain recovered capacity.</td><td>No leakage
Capacity recovery rate ≥ 80% (of C_{nom} in 2.1)</td></tr>
<tr><td rowspan="3">4.3.4
Temperature Dependency of Capacity</td><td colspan="2">Cells shall be charged per 4.1.1 at 23ºC ± 2ºC and discharged per 4.1.2 at the following temperatures.</td><td></td></tr>
<tr><td>Charge</td><td>Discharge</td><td>Capacity</td></tr>
<tr><td>23℃</td><td>-10℃
0℃
23℃
60℃</td><td>60% (of C_{nom} in 2.1)
80% (of C_{nom} in 2.1)
100% (of C_{nom} in 2.1)
95% (of C_{nom} in 2.1)</td></tr>
</table>

4.4 Mechanical Specification

Item	Condition	Specification
4.4.1 Drop Test	Cells charged per 4.1.1 are dropped onto an oak board from 1 meter height for 1 cycle, 2 drops from each cell terminal and 1 drop from side of cell. (Total number of drops =3).	No leakage No temperature rising
4.4.2 Vibration Test	Cells charged per 4.1.1 are vibrated for 90 minutes per each of the three mutually perpendicular axes (x, y, z) with total excursion of 0.8mm, frequency of 10Hz to 55Hz and sweep of 1Hz change per minute.	No leakage

4.5 Safety Specification

Item	Condition	Specification
4.5.1 Overcharge Test	Cells are discharged per 4.1.2, then charged at constant current of 3 times the max. Charge condition and constant voltage of 4.2V while tapering the charge current. Charging is continued for 7 hours (Per UL1642).	No explosion, No fire
4.5.2 External Short - Circuiting Test	Cells are charged per 4.1.1, and the positive and negative terminal is connected by a 100 mΩ-wire for 1 hour (Per UL1642).	No explosion, No fire

4,5.3 Overdischarge Test	Cells are discharged at constant current of 0.2C to 250% of the minimum capacity.	No explosion, No fire
4.5.4 Heating Test	Cells are charged per 4.1.1 and heated in a circulating air oven at a rate of 5ºC per minute to 130ºC. At 130ºC, oven is to remain for 10 minutes before test is discontinued (Per UL1642).	No explosion, No fire
4.5.5 Impact Test	Cells charged per 4.1.1 are impacted with their longitudinal axis parallel to the flat surface and perpendicular to the longitudinal axis of the 15.8mm diameter bar (Per UL1642).	No explosion, No fire
4.5.6 Crush Test	Cells charged per 4.1.1 are crushed with their longitudinal axis parallel to the flat surface of the crushing apparatus (Per UL1642).	No explosion, No fire

5. Caution

Warning for using the lithium ion rechargeable battery. Mishandling of the battery may cause heat, fire and deterioration in performance. Be sure to observe the following.

5.1 Cautions for Use and Handling

- When using the application equipped with the battery, refer to the user’s manual before usage.
- Please read the specific charger manual before charging.
- Charge time should not be longer than specified in the manual.
- When the cell is not charged after long exposure to the charger, discontinue charging.
- Battery must be charged at operating temperature range 0 ~ 45℃.
- Battery must be discharged at operating temperature range -20 ~ 60℃.
- Please check the positive (+) and negative (-) direction before packing.
- When a lead plate or wire is connected to the cell for packing, check out insulation not to short-circuit.
- Battery must be stored separately.
- Battery must be stored in a dry area with low temperature for long-term storage.
- Do not place the battery in direct sunlight or heat.
- Do not use the battery in high static energy environment where the protection device can be damaged.
- When rust or smell is detected on first use, please return the product to the seller immediately.
- The battery must be away from children or pets
- When cell life span shortens after long usage, please exchange to new cells.

5.2 Prohibitions

- Do not use different charger. Do not use cigarette jacks (in cars) for charging.
- Do not charge with constant current more than maximum charge current.
- Do not disassemble or reconstruct the battery.
- Do not throw or cause impact.
- Do not pierce a hole in the battery with sharp things. (such as nail, knife, pencil, drill)
- Do not use with other batteries or cells.
- Do not solder on battery directly.
- Do not press the battery with overload in manufacturing process, especially ultrasonic welding.
- Do not use old and new cells together for packing.
- Do not expose the battery to high heat. (such as fire)
- Do not put the battery into a microwave or high pressure container.
- Do not use the battery reversed.
- Do not connect positive(+) and negative(-) with conductive materials (such as metal, wire)
- Do not allow the battery to be immerged in or wetted with water or sea-water.

5.3 Caution for the battery and the pack

Pack shall meet under condition to maintain battery safety and last long performance of the lithium rechargeable cells.

5.3.1 Installing the battery into the pack

-. The cell should be inspected visually before battery assembly into the pack.

-. Damaged cell should not be used. (damaged surface, can-distortion, electrolyte-smell)

-. Different Lot Number cells should not be packaged into the same pack.

-. Different types of cells, or same types but different cell maker's should not be used together.

5.3.2 Design of battery pack

-. The battery pack should not be connected easily to any charger other than the dedicated charger.

-. The battery pack has function not to cause external short cut easily.

5.3.3 Charge

-. Charging method is Constant Current-Constant Voltage (CC/CV).

-. Charging should be operating under maximum charge voltage and current which is specified in the product specification. (Article. 2.4, 2.5)

-. The battery should be charged under operating temperature specified in product specification. (Article. 2.9)

5.3.4 Discharge

-. Discharging method is Constant Current (CC).

-. Discharging should be operating under maximum discharge current which is specified in the product specification. (Article. 2.7)

-. Discharging should be done by cut off voltage which is specified in the product specification. (Article. 2.6)

-. The battery should be discharged under operating temperature specified in product specification. (Article. 2.9)

5.3.5 Protection Circuit

-. The protection circuit should be installed in the battery pack, charger.

-. Charger or pack should have voltage sensing system to control over charge or discharge in order to maintain the battery's normal operating mode and protect cell imbalance.

-. Charger or pack should have warning system for over temperature, over voltage and over current.

EXHIBIT 5

PRODUCT SPECIFICATION

Rechargeable Lithium Ion Battery
Model : 20650 HG6 3000mAh

LG Chem

20 YOIDO-DONG YOUNGDUNGPO-GU,

SEOUL 190-721, KOREA

http://www.lgchem.com

Revision History

Revision	Date	Originator	Description
0	2019-01-25	Philip Park	- Original Release

Contents

1. General Information

1.1 Scope

This product specification defines the requirements of the rechargeable lithium ion battery to be supplied to the customer by LG Chem.

1.2 Application: Power Tools, Vacuum Cleaner, Garden tool

1.3 Product classification: Cylindrical rechargeable lithium ion battery

1.4 Model name: 20650 HG6

2. Nominal Specification

Item	Condition / Note	Specification
2.1 Capacity	Std. charge / discharge	Nominal 3,000 mAh (C_{nom}) Minimum 2,900 mAh (C_{min})
2.2 Nominal Voltage	Average for Std. discharge	3.6V
2.3.1 Standard Charge (Refer to 4.1.1)	Constant current Constant voltage End condition(Cut off)	1.5A 4.2V 50mA
2.3.2 Fast charge (Refer to 4.1.3)	Constant current Constant voltage End condition(Cut off)	4A 4.2V 100mA
2.4 Max. Charge Voltage	-	4.2V
2.5 Max. Charge Current	-	4A
2.6.1 Standard Discharge (Refer to 4.1.2)	Constant current End voltage(Cut off)	600mA 2.0V
2.6.2 Fast Discharge (Refer to 4.1.3)	Constant current End voltage(Cut off)	10A, 20A 2.0V
2.7 Max. Discharge Current	For continuous discharge	30A
2.8 Weight	Max.	58 g
2.9 Operating Temperature (Cell Surface Temperature)	Charge Discharge	0 ~ 50℃ -20 ~ 75℃
2.10 Storage Temperature (for shipping state[i])	1 month 3 month 1 year	-20 ~ 60℃ -20 ~ 45℃ -20 ~ 25℃

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* Shipping state : About 40% capacity of fully charged state

3. Appearance and Dimension

3.1 Appearance

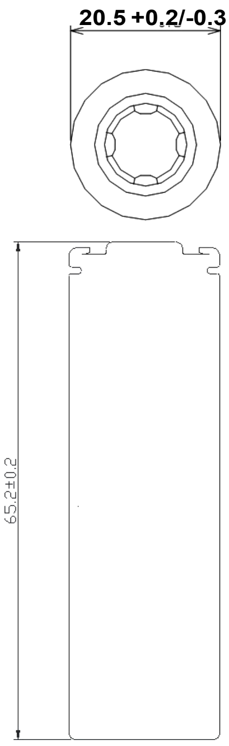
There shall be no such defects as deep scratch, crack, rust, discoloration or leakage, which may affect the commercial value of the cell.

3.2 Dimension

Diameter : 20.5 + 0.2/-0.3 mm (Max. 20.7 mm)

Diameter is defined as the largest data value measured on the "A" area of a cylindrical cell.

Height : 65.2 ± 0.2 mm (Max. 65.4 mm)



4. Performance Specification

4.1 Standard test condition

4.1.1 Standard Charge

Unless otherwise specified, "Standard Charge" shall consist of charging at constant current of 1.5A. The cell shall then be charged at constant voltage of 4.2V while tapering the charge current. Charging shall be terminated when the charging current has tapered to 50mA. For test purposes, charging shall be performed at 25ºC ± 2ºC.

4.1.2 Standard Discharge

"Standard Discharge" shall consist of discharging at a constant current of 600mA to 2.0V. Discharging is to be performed at 25 ºC ± 2 ºC unless otherwise noted (such as capacity versus temperature).

4.1.3 Fast Charge / Discharge condition

Cells shall be charged at constant current of 4A to 4.2V with end current of 100mA. Cells shall be discharged at constant current of 10A and 20A to 2.0V. Cells are to rest 10 minutes after charge and 60 minutes after discharge.

4.2 Electrical Specification

Item	Condition	Specification
4.2.1 Initial AC Impedance	Cell shall be measured at 1kHz after charge per 4.1.1.	≤ 19 mΩ, without PTC
4.2.2 Initial Capacity	Cell shall be charged per 4.1.1 and discharged per 4.1.2 within 1h after full charge.	3000 mAh (C_{nom})
4.2.3 Cycle Life	Cells shall be charged and discharged per 4.1.3, 300 cycles(10A) and 200 cycles(20A) .A cycle is defined as one charge and one discharge. 301st (10A) and 201st (19A) discharge capacity shall be measured per 4.1.1 and 4.1.2	≥ 60 % (of C_{nom} in 2.1)

4.3 Environmental specification.

Item	Condition	Specification
4.3.1 Storage Characteristics	Cells shall be charged per 4.1.1 and stored in a temperature-controlled environment at 23ºC ± 2ºC for 30 days. After storage, cells shall be discharged per 4.1.2 to obtain the remaining capacity*.	Capacity remaining rate ≥ 90% (of C_{nom} in 2.1)
4.3.2 High Temperature Storage Test	Cells shall be charged per 4.1.1 and stored in a temperature-controlled environment at 60ºC for 1 week. After storage, cells shall be discharged per 4.1.2 and cycled per 4.1.1 and 4.1.2 for 3 cycles to obtain recovered capacity*.	No leakage, Capacity recovery rate ≥ 80% (of C_{nom} in 2.1)

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* Remaining Capacity : After storage, cells shall be discharged with standard condition(4.1.2) to measure the remaining capacity.

** Recovery Capacity : After storage, cells shall be discharged with standard discharge condition(4.1.2), and then cells shall be charged with standard charge condition(4.1.1), and then discharged with standard discharge condition(4.1.2). This charge / discharge cycle shall be repeated three times to measure the recovery capacity.

<table>
<tr><td>4.3.3
Thermal Shock Test</td><td colspan="2">72ºC (6h) ← 0.5hrs → -40ºC (6h) for 10 cycles with cells charged per 4.1.1 After test, cells voltage are measured.(Per UN38.3)</td><td>No leakage, no venting
Voltage ≥ 90% (of initial voltage)</td></tr>
<tr><td rowspan="6">4.3.4
Temperature Dependency of Capacity</td><td colspan="2">Cells shall be charged per 4.1.1 at 25ºC ± 2ºC and discharged per 4.1.2 at the following temperatures.</td><td></td></tr>
<tr><td>Charge</td><td>Discharge</td><td>Capacity</td></tr>
<tr><td rowspan="4">25℃</td><td>-10℃</td><td>60% (of C_{nom} in 2.1)</td></tr>
<tr><td>0℃</td><td>80% (of C_{nom} in 2.1)</td></tr>
<tr><td>23℃</td><td>100% (of C_{nom} in 2.1)</td></tr>
<tr><td>60℃</td><td>95% (of C_{nom} in 2.1)</td></tr>
</table>

4.4 Mechanical Specification

Item	Condition	Specification
4.4.1 Drop Test	Cells charged per 4.1.1 are dropped onto an oak board from 1 meter height for 1 cycle, 2 drops from each cell terminal and 1 drop from side of cell. (Total number of drops =3).	No leakage No temperature rising
4.4.2 Vibration Test	Cells charged per 4.1.1 are vibrated for 90 minutes per each of the three mutually perpendicular axes (x, y, z) with total excursion of 0.8mm, frequency of 10Hz to 55Hz and sweep of 1Hz change per minute.	No leakage

4.5 Safety Specification

Item	Condition	Specification
4.5.1 Overcharge Test	Cells are discharged per 4.1.2, then charged at constant current of 3 times the max. charge condition and constant voltage of 4.2V while tapering the charge current. Charging is continued for 7 hours (Per UL1642).	No explosion, No fire
4.5.2 External Short - Circuiting Test	Cells are charged per 4.1.1, and the positive and negative terminal is connected by a 100 mΩ-wire for 1 hour (Per UL1642).	No explosion, No fire
4,5.3 Overdischarge Test	Cells are discharged at constant current of 0.2C to 250% of the minimum capacity.	No explosion, No fire

4.5.4 Heating Test	Cells are charged per 4.1.1 and heated in a circulating air oven at a rate of 5ºC per minute to 130ºC. At 130ºC, oven is to remain for 10 minutes before test is discontinued (Per UL1642).	No explosion, No fire
4.5.5 Impact Test	Cells charged per 4.1.1 are impacted with their longitudinal axis parallel to the flat surface and perpendicular to the longitudinal axis of the 19.8mm diameter bar (Per UL1642, UN38.3).	No explosion, No fire
4.5.6 Crush Test	Cells charged per 4.1.1 are crushed with their longitudinal axis parallel to the flat surface of the crushing apparatus (Per UL1642).	No explosion, No fire

5. Caution and Prohibition in Handling

Warning for using the lithium ion rechargeable battery. Mishandling of the battery may cause heat, fire and deterioration in performance. Be sure to observe the following.

Caution

- When using the application equipped with the battery, refer to the user’s manual before usage.
- Please read the specific charger manual before charging.
- When the cell is not charged after long exposure to the charger, discontinue charging.
- Battery must be charged at operating temperature range 0 ~ 50℃.
- Battery must be discharged at operating temperature(cell surface temperature) range -20 ~ 75℃.
- Please check the positive(+) and negative(-) direction before packing.
- When a lead plate or wire is connected to the cell for packing, check out insulation not to short-circuit.
- Battery must be stored separately.
- Battery must be stored in a dry area with low temperature for long-term storage.
- Do not place the battery in direct sunlight or heat.
- Do not use the battery in high static energy environment where the protection device can be damaged.
- When rust or smell is detected on first use, please return the product to the seller immediately.
- The battery must be away from children or pets
- When cell life span shortens after long usage, please exchange to new cells.

Prohibitions

- Do not use different charger. Do not use cigarette jacks (in cars) for charging.
- Do not charge with constant current more than maximum charge current.
- Do not disassemble or reconstruct the battery.
- Do not throw or cause impact.
- Do not pierce a hole in the battery with sharp things. (such as nail, knife, pencil or drill, etc.)
- Do not use with other batteries or cells.
- Do not solder on battery directly.
- Do not press the battery with overload in manufacturing process, especially ultrasonic welding.
- Do not use old and new cells together for packing.
- Do not expose the battery to high heat. (such as fire)
- Do not put the battery into a microwave or high pressure container.
- Do not use the battery reversed.
- Do not connect positive(+) and negative(-) with conductive materials (such as metal, wire)
- Do not allow the battery to be immerged in or wetted with water or sea-water.

EXHIBIT 6

PRODUCT SPECIFICATION
CONFIDENTIAL

Prepared		*Document No.*	*Date*	*Rev*
LGC MBD/MBDC	Oh, Kyung Su	LRB-PS-CY3450_MJ1	2014-08-22	1
Approved		*Description*		
LGC MBD/MBDC	Kim, Dong Myung	Lithium Ion INR18650 MJ1 3500mAh		

PRODUCT SPECIFICATION

Rechargeable Lithium Ion Battery
Model : INR18650 MJ1 3500mAh

20　YOIDO-DONG YOUNGDUNGPO-GU,
SEOUL 150-721, KOREA
http://www.lgchem.com

Revision History

Revision	Date	Originator	Description
0	2014-04-28	Oh, Kyung Su	- Draft
1	2014-08-22	Oh, Kyung Su	-2.2. Nominal Voltage - 3.63V → 3.635V

Contents

1. General Information

1.1 Scope

This product specification defines the requirements of the rechargeable lithium ion battery of LG Chem.

1.2 Product classification

Cylindrical rechargeable lithium ion battery

1.3 Model name

INR18650 MJ1

2. Nominal Specification

Item	Condition / Note	Specification
2.1 Energy	Std. charge / discharge	Nominal 3500 mAh Minimum 3400 mAh
2.2 Nominal Voltage	Average	3.635V
2.3 Standard Charge (Refer to 4.1.1)	Constant current Constant voltage End current(Cut off)	0.5C (1700mA) 4.2V 50mA
2.4 Max. Charge Voltage		4.2 ± 0.05V
2.5 Max. Charge Current		1.0 C (3400mA)
2.6 Standard Discharge (Refer to 4.1.2)	Constant current End voltage(Cut off)	0.2C (680mA) 2.5V
2.7 Max. Discharge Current		10A
2.8 Weight	Approx.	Max. 49.0 g
2.9 Operating Temperature	Charge Discharge	0 ~ 45℃ -20 ~ 60℃
2.10 Storage Temperature (for shipping state)	1 month 3 month 1 year	-20 ~ 60℃ -20 ~ 45℃ -20 ~ 20℃

3. Appearance and Dimension

3.1 Appearance

There shall be no such defects as deep scratch, crack, rust, discoloration or leakage, which may adversely affect the commercial value of the cell.

3.2 Dimension

Diameter: 18.4 +0.1 / -0.3 mm (Max. 18.5mm)
Height: 65.0 ±0.2mm (Max. 65.2mm)

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4. Performance Specification

4.1 Standard test condition

4.1.1 Standard Charge

Unless otherwise specified, “Standard Charge” shall consist of charging at constant current of 0.5C. The cell shall then be charged at constant voltage of 4.20V while tapering the charge current. Charging shall be terminated when the charging current has tapered to 50mA. For test purposes, charging shall be performed at 23ºC ± 2ºC.

4.1.2 Standard Discharge

“Standard Discharge” shall consist of discharging at a constant current of 0.2C to 2.50V. Discharging is to be performed at 23 ºC ± 2 ºC unless otherwise noted (such as capacity versus temperature).

4.1.3 High Drain rate Charge/discharge condition

Cells shall be charged at constant current of 1,500mA to 4.20V with end current of 100mA. Cells shall be discharged at constant current of 4,000mA to 2.50V. Cells are to rest 10 minutes after charge and 20 minutes after discharge.

4.2 Electrical Specification

Item	Condition	Specification
4.2.1 Initial AC Impedance	Cell shall be measured at 1kHz after charge per 4.1.1.	≤ 40 mΩ, without PTC
4.2.2 Initial Capacity	Cells shall be charged per 4.1.1 and discharged per 4.1.2 within 1h after full charge.	≥ 3400 mAh
4.2.3 Cycle Life	Cells shall be charged and discharged per 4.1.3 400 cycles. A cycle is defined as one charge and one discharge. 401st discharge power shall be measured per 4.1.1 and 4.1.2	≥ 80 % (of C_{min} in 2.1)

4.3 Environmental specification.

<table>
<tr><th>Item</th><th colspan="2">Condition</th><th>Specification</th></tr>
<tr><td>4.3.1
Storage Characteristics</td><td colspan="2">Cells shall be charged per 4.1.1 and stored in a temperature-controlled environment at 23ºC ± 2ºC for 30 days. After storage, cells shall be discharged per 4.1.2 to obtain the remaining power*.</td><td>Power remaining rate ≥ 90% (P_{min} in 2.1)</td></tr>
<tr><td>4.3.2
High Temperature Storage Test</td><td colspan="2">Cells shall be charged per 4.1.1 and stored in a temperature-controlled environment at 60ºC for 1 week. After storage, cells shall be discharged per 4.1.2 and cycled per 4.1.3 for 3 cycles to obtain recovered power**.</td><td>No leakage,
Power recovery rate ≥ 80%</td></tr>
<tr><td>4.3.3
High Temperature and High Humidity Test</td><td colspan="2">Cells are charged per 4.1.1 and stored at 60ºC (95% RH) for 168 hours. After test, cells are discharged per 4.1.2 and cycled per 4.1.3 for 3 cycles to obtain recovered power.</td><td>No leakage, No rust
Power recovery rate ≥ 80%</td></tr>
<tr><td>4.3.4
Thermal Shock Test</td><td colspan="2">65ºC (8h) ← 3hrs → -20ºC (8h) for 8 cycles with cells charged per 4.1.1 After test, cells are discharged per 4.1.2 and cycled per 4.1.3 for 3 cycles to obtain recovered power.</td><td>No leakage
Power recovery rate ≥ 80%</td></tr>
<tr><td rowspan="6">4.3.5
Temperature Dependency of Capacity</td><td colspan="2">Cells shall be charged per 4.1.1 at 23ºC ± 2ºC and discharged per 4.1.2 at the following temperatures.</td><td></td></tr>
<tr><td>Charge</td><td>Discharge</td><td>Capacity</td></tr>
<tr><td rowspan="4">23℃</td><td>-10℃</td><td>70% of P_{ini}</td></tr>
<tr><td>0℃</td><td>80% of P_{ini}</td></tr>
<tr><td>23℃</td><td>100% of P_{ini}</td></tr>
<tr><td>60℃</td><td>95% of P_{ini}</td></tr>
</table>

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* Remaining Capacity: After storage, cells shall be discharged with Std. condition (4.1.2) to measure the remaining capacity.

** Recovery Capacity: After storage, cells shall be discharged with fast discharge condition (4.1.3), and then cells shall be charged with std. charge condition (4.1.1), and then discharged with Std. condition (4.1.2). This charge / discharge cycle shall be repeated three times to measure the recovery capacity.

4.4 Mechanical Specification

Item	Condition	Specification
4.4.1 Drop Test	Cells charged per 4.1.1 are dropped onto an wooden floor from 1.0 meter height for 1 cycle, 2 drops from each cell terminal and 1drop from the side of cell can (Total number of drops = 3).	No leakage No temperature rising
4.4.2 Vibration Test	Cells charged per 4.1.1 are vibrated for 90 minutes per each of the three mutually perpendicular axis (x, y, z) with total excursion of 0.8mm, frequency of 10Hz to 55Hz and sweep of 1Hz change per minute	No leakage

4.5 Safety Specification

Item	Condition	Specification
4.5.1 Overcharge Test	Cells are discharged per 4.1.2, and then charged at constant current of 3 times the max. charge condition and constant voltage of 4.2V while tapering the charge current. Charging is continued for 7 hours (Per UL1642).	: No explode, No fire
4.5.2 External Short - Circuiting Test	Cells are charged per 4.1.1, and the positive and negative terminal is connected by a 100mΩ-wire for 1 hour (Per UL1642).	: No explode, No fire
4,5.3 Overdischarge Test	Cells are discharged at constant current of 0.2C to 250% of the minimum capacity.	: No explode, No fire
4.5.4 Heating Test	Cells are charged per 4.1.1 and heated in a circulating air oven at a rate of 5ºC per minute to 130ºC. At 130ºC, oven is to remain for 10 minutes before test is discontinued (Per UL1642).	: No explode, No fire
4.5.5 Impact Test	Cells charged per 4.1.1 are impacted with their longitudinal axis parallel to the flat surface and perpendicular to the longitudinal axis of the 15.8mm diameter bar (Per UL1642).	: No explode, No fire
4.5.6 Crush Test	Cells charged per 4.1.1 are crushed with their longitudinal axis parallel to the flat surface of the crushing apparatus (Per UL1642).	: No explode, No fire

5. Caution

Warning: Using the lithium ion rechargeable battery, mishandling of the battery may cause heat, fire and deterioration in performance. Be sure to observe the following.

5.1 Cautions for Using and Handling

- When using the application equipped with the battery, refer to the user's manual before usage.
- Please read the specific charger manual before charging.
- Charge time should not be longer than specified in the manual.
- When the cell is not charged after long exposure to the charger, discontinue charging.
- Battery must be charged at operating temperature range 0 ~ 45℃.
- Battery must be discharged at operating temperature range -20 ~ 60℃.
- Please check the positive(+) and negative(-) direction before packing.
- When a lead plate or wire is connected to the cell for packing, check out insulation not to short-circuit.
- Battery must be stored separately.
- Battery must be stored in a dry area with low temperature for long-term storage.
- Do not place the battery in direct sunlight or heat.
- Do not use the battery in high static energy environment where the protection device can be damaged.
- When rust or smell is detected on first use, please return the product to the seller immediately.
- The battery must be away from children or pets
- When cell life span shortens after long usage, please exchange to new cells.

5.2 Prohibitions

- Do not use different charger. Do not use cigarette jacks (in cars) for charging.
- Do not charge with constant current more than maximum charge current.
- Do not disassemble or reconstruct the battery.
- Do not throw or cause impact.
- Do not pierce a hole in the battery with sharp things. (such as nail, knife, pencil, drill)
- Do not use with other batteries or cells.
- Do not solder on battery directly.
- Do not press the battery with overload in manufacturing process, especially ultrasonic welding.
- Do not use old and new cells together for packing.
- Do not expose the battery to high heat. (such as fire)
- Do not put the battery into a microwave or high pressure container.
- Do not use the battery reversed.
- Do not connect positive(+) and negative(-) with conductive materials (such as metal, wire)
- Do not allow the battery to be immerged in or wetted with water or sea-water.

5.3 Caution for the battery and the pack

Pack shall meet under condition to maintain battery safety and last long performance of the lithium rechargeable cells.

5.3.1 Installing the battery into the pack

-. The cell should be inspected visually before battery assembly into the pack.

-. Damaged cell should not be used. (Damaged surface, can-distortion, electrolyte-smell)

-. Different Lot Number cells should not be packaged into the same pack.

-. Different types of cells, or same types but different cell maker's should not be used together.

5.3.2 Design of battery pack

-. The battery pack should not be connected easily to any charger other than the dedicated charger.

-. The battery pack has function not to cause external short cut easily.

5.3.3 Charge

-. Charging method is Constant Current-Constant Voltage (CC/CV).

-. Charging should be operating under maximum charge voltage and current which is specified in the product specification. (Article. 2.4, 2.5)

-. The battery should be charged under operating temperature specified in the product specification. (Article. 2.9)

5.3.4 Discharge

-. Discharging method is Constant Current (CC).

(In case of using the battery for mobile equipment, discharging mode could be Constant Power.)

-. Discharging should be operating under maximum discharge current which is specified in the product specification. (Article. 2.7)

-. Discharging should be done by cut off voltage which is specified in the product specification. (Article. 2.6)

-. The battery should be discharged under operating temperature specified in the product specification. (Article. 2.9)

5.3.5 Protection Circuit

-. The protection circuit should be installed in the battery pack, charger.

-. Charger or pack should have voltage sensing system to control over charge or discharge in order to maintain the battery's normal operating mode and protect cell imbalance.

-. Charger or pack should have warning system for over temperature, over voltage and over current.

6. EXCLUSION OF LIABILITY

THE WARRANTY SHALL NOT COVER DEFECTS CAUSED BY NORMAL WEAR AND TEAR, INADEQUATE MAINTENANCE, HANDLING, STORAGER FAULTY REPAIR, MODIFICATION TO THE BATTERY OR PACK BY A THIRD PARTY OTHER THAN LGC OR LGC'S AGENT APPROVED BY LGC, FAILURE TO OBSERVE THE PRODUCT SPECIFICATION PROVIDED HEREIN OR IMPROPER USE OR INSTALLATION, INCLUDING BUT NOT LIMITED TO, THE FOLLOWING:

-. DAMAGE DURING TRANSPORT OR STORAGE
-. INCORRECT INSTALLATION OF BATTERY INTO PACK OR MAINTENANCE
-. USE OF BATTERY OR PACK IN INAPPROPRIATE ENVIRONMENT
-. IMPROPER, INADEQUATE, OR INCORRECT CHARGE, DISCHARGE OR PRODUCTION CIRCUIT OTHER THAN STIPULATED HEREIN
-. INCORRECT USE OR INAPPROPRIATE USE
-. INSUFFICIENT VENTILATION
-. IGNORING APPLICABLE SAFETY WARNINGS AND INSTRUCTIONS
-. ALTERING OR ATTEMPTED REPAIRS BY UNAUTHORIZED PERSONNEL
-. IN CASE OF FORCE MAJEURE (LIGHTENING, STORM, FLOOD, FIRE, EARTHQUAKE, ETC.)

THERE ARE NO WARRANTIES – IMPLIED OR EXPRESS – OTHER THAN THOSE STIPULATED HEREIN. LG CHEM SHALL NOT BE LIABLE FOR ANY CONSEQUENTIAL OR INDIRECT DAMAGES ARISING OR IN CONNECTION WITH THE PRODUCT SPECIFICATION, BATTERY OR PACK.

Complaints

1:99-mc-09999 Plaintiff(s) v. Defendant(s)

U.S. District Court

District of Delaware

Notice of Electronic Filing

The following transaction was entered by Farnan, Michael on 8/29/2022 at 2:38 PM EDT and filed on 8/29/2022

Case Name: Plaintiff(s) v. Defendant(s)
Case Number: 1:99-mc-09999
Filer:
Document Number: 931

Docket Text:
COMPLAINT - Molecular Rebar Design, LLC and Black Diamond Structures, LLC v. LG Chem, Ltd., LG Energy Solution, Ltd., LG Energy Solution Michigan, Inc., and LG Electronics, Inc.. Filing fee $ 402, receipt number ADEDC-3946925. (Attachments: # (1) Exhibit 1, # (2) Exhibit 2, # (3) Exhibit 3, # (4) Exhibit 4, # (5) Exhibit 5, # (6) Exhibit 6, # (7) Civil Cover Sheet, # (8) Patent/Trademark Report, # (9) Rule 7.1 Disclosure Statement, # (10) Summons Forms - Unsigned)(Farnan, Michael)

1:99-mc-09999 Notice has been electronically mailed to:

1:99-mc-09999 Filer will deliver document by other means to:

The following document(s) are associated with this transaction:

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