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## (12) United States Patent

Hellring et al.

(54) ELECTRODE SLURRY COMPOSITION FOR LITHIUM ION ELECTRICAL STORAGE DEVICES

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See application file for complete search history.

#### (56) References Cited

#### U.S. PATENT DOCUMENTS

6,168,885 B1 1/2001 Narang et al. 9,273,399 B2 3/2016 Hellring et al. (Continued)

#### FOREIGN PATENT DOCUMENTS

CN 1331252 C 8/2007 CN 103715393 A 4/2014 (Continued)

#### OTHER PUBLICATIONS

"New Polymer Synthesis and Preparation Technology", Chemistry and Chemical Engineering Excellent Series Books, Harbin Institute of Technology Press, Zhen Hu, Chunhua Zhang, Yan Liang.

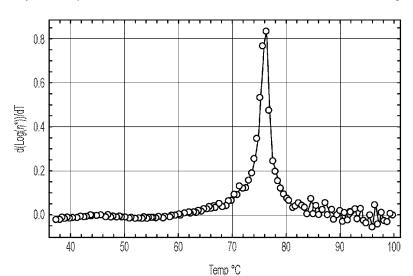
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#### (57) ABSTRACT

The present invention provides a slurry composition comprising (a) a binder comprising a polymer comprising a fluoropolymer dispersed in a liquid medium; and (b) at least one conductive carbon material having a BET surface area of greater than  $100~\rm m^2/g$ . Also provided are electrodes and electrical storage devices.

#### 20 Claims, 2 Drawing Sheets



#### Related U.S. Application Data FOREIGN PATENT DOCUMENTS continuation of application No. 16/629,203, filed as CN CN 104497190 A 4/2015 application No. PCT/US2018/041075 on Jul. 6, 2018, 105612641 A 5/2016 CN106299379 A 1/2017 now Pat. No. 11,424,451. CN 106463732 A 2/2017 EP 3324468 A 5/2018 JP H10172573 A 6/1998 (60) Provisional application No. 62/529,524, filed on Jul. JP H11329904 A 11/1999 7, 2017. JP 2000150320 A 5/2000 JP 2000182606 A 6/2000 (51) Int. Cl. JP JP 2002260666 A 9/2001 2003257433 A 9/2003 H01M 4/505 (2010.01)2003317722 A JP 11/2003 H01M 4/525 (2010.01)JP 2004071566 A 3/2004 H01M 4/62 (2006.01)JP 2007273639 A 10/2007 H01M 4/66 (2006.01)JP 4325002 B2 9/2009 JP 2010049872 A 3/2010 (52) U.S. Cl. 2013084351 A JP 5/2013 H01M 4/505 (2013.01); H01M 4/525 CPC ..... JР 2014132591 A 7/2014 (2013.01); H01M 4/625 (2013.01); H01M 2014181252 A JP 9/2014 4/661 (2013.01) JP 2016181479 A 10/2016 JP 2016201244 A 12/2016 KR 20020092029 A 12/2002 (56)References Cited 20060037618 A 5/2006 KR KR 20140019357 A 2/2014 U.S. PATENT DOCUMENTS KR 20160007413 A 1/2016 2016-0046882 A 4/2016 KR 7/2016 Hellring et al. 9,385,374 B2 20160082503 A 7/2016 KR 9,466,830 B1 10/2016 Shan et al. 20160139240 A 12/2016 KR 9,761,903 B2 9/2017 Hellring et al. TW 200410439 A 6/2004 10,033,043 B2 7/2018 Hellring et al. WO 2000049103 A1 8/2000 10,388,961 B2 8/2019 Fukumine et al. WO 2008129041 A1 10/2008 10,619,070 B2 4/2020 Kobayashi et al. WO 2009063907 A1 5/2009 10,763,490 B2 9/2020 Daughenbaugh et al. WO 2012124582 A1 9/2012 Hellring et al. 10,964,949 B2 3/2021 WO 2013183717 A1 12/2013 11,228,037 B2 1/2022 Huang et al. 2015-064099 A1 5/2015 WO 11,764,361 B2 9/2023 Hellring et al. 2015064999 A1 5/2015 WO 2010/0266882 A1 10/2010 Igarashi et al. 2015153583 A1 WO 6/2015 2010/0304270 A1 12/2010 Amin-Sanayei et al. WO 2016190666 A1 12/2016 2011/0318638 A1 12/2011 Koh et al. WO 2017010093 A1 1/2017 2014/0227593 A1 8/2014 Lee et al. 2017056974 A1 4/2017 2015/0099171 A1 4/2015 Alarco et al. 2015/0200398 A1 7/2015 Yeou et al. 2017/0110733 A1 4/2017 Yoon et al. OTHER PUBLICATIONS 2017/0226365 A1 8/2017 Kobayashi et al. 2017/0324096 A1\* ..... H01M 4/525 11/2017 Korchev ..... "Green Plasticizers", Scientific and Technical Documentation Press, 2018/0048027 A1 2/2018 Itakura et al. Beijing China, Oct. 2011, Duoren Wang. 2018/0114988 A1 4/2018 Yoon et al. Machine English translation of the abstract of WO2012124582A1. 2018/0269484 A1 9/2018 Kobayashi et al. Machine English translation of the abstract of CN104497190A. 2020/0136146 A1 4/2020 Hellring et al. Machine English translation of the abstract of CN1331252C Hellring et al. 2020/0176777 A1 6/2020 ASTM Designation: D 3539—87 (Reapproved 1996). Standard Test 9/2020 Hellring et al. 2020/0295373 A1 Methods for Evaporation Rates of Volatile Liquids by Shell Thin-2021/0242447 A1 8/2021 Jiang et al. Film Evaporometer (Year: 1996). 2024/0030447 A1 1/2024 Hellring et al. 2024/0055612 A1 2/2024 Hellring et al.

\* cited by examiner

2024/0120491 A1

4/2024 Hellring et al.

Figure 1

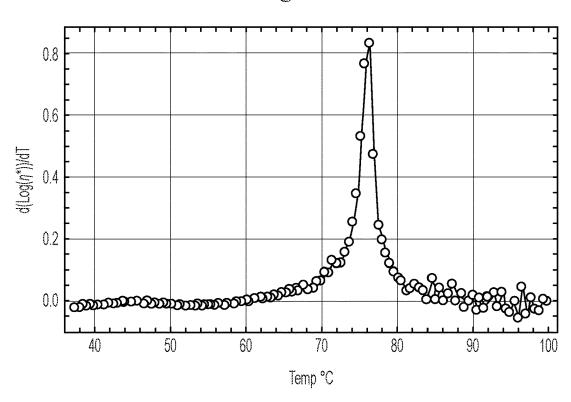


Figure 2

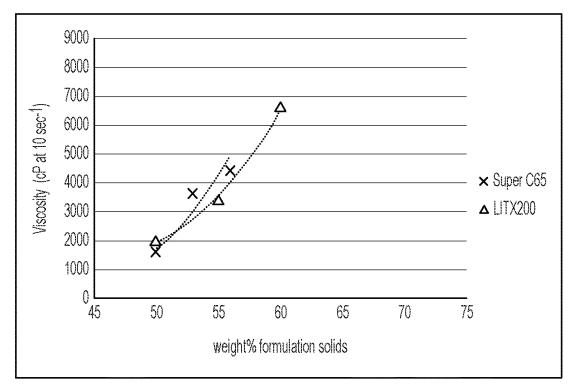


Figure 3

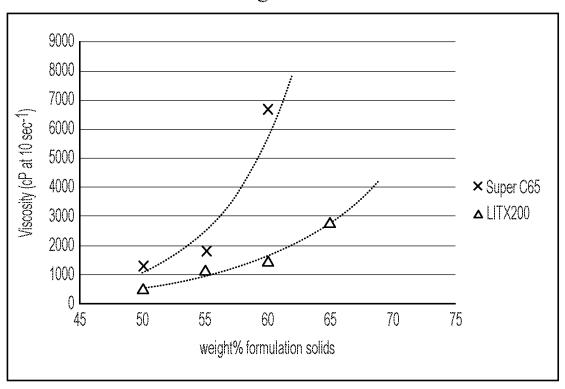
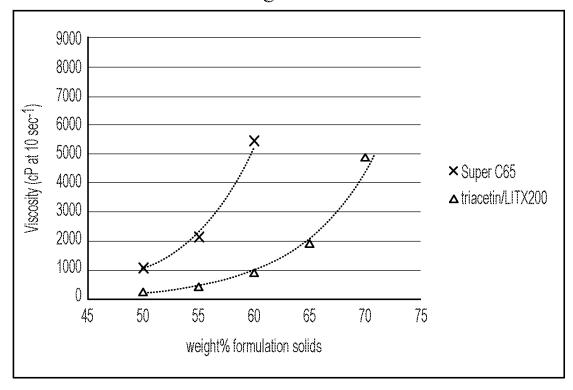


Figure 4



# ELECTRODE SLURRY COMPOSITION FOR LITHIUM ION ELECTRICAL STORAGE DEVICES

## CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. application Ser. No. 17/862,121, filed on Jul. 11, 2022, that claimed the benefit of U.S. application Ser. No. 16/629,203, filed on Jan. 10, 2020, as a national stage entry of Int'l App. Ser. No. PCT/US2018/041075, filed on Jul. 6, 2018, that claimed the benefit of U.S. Prov. App. Ser. No. 62/529,524, filed on Jul. 7, 2017, each of which are incorporated herein by reference.

#### FIELD OF THE INVENTION

The invention relates to fluoropolymer compositions that include conductive carbon materials having a surface area greater than  $100~\text{m}^2/\text{g}$ .

#### BACKGROUND OF THE INVENTION

There is a trend in the electronics industry to produce smaller devices, powered by smaller and lighter batteries. 25 Batteries with a negative electrode—such as a carbonaceous material, and a positive electrode—such as lithium metal oxides can provide relatively high power and low weight.

Polyvinylidene fluoride, because of its excellent electrochemical resistance, has been found to be a useful binder for 30 forming electrodes to be used in electrical storage devices. Typically, the polyvinylidene fluoride is dissolved in an organic solvent and the electrode material, that is, the electrical active lithium compound and a carbonaceous material, is combined with the PVDF solution to form a 35 slurry that is applied to a metal foil or mesh to form the electrode.

The role of the organic solvent is to dissolve PVDF in order to provide good adhesion between the electrode material particles and the metal foil or mesh upon evaporation of 40 the organic solvent. Currently, the organic solvent of choice is N-methyl-2-pyrrolidone (NMP). PVDF binders dissolved in NMP provide superior adhesion and an interconnectivity of all the active ingredients in the electrode composition. The bound ingredients are able to tolerate large volume 45 expansion and contraction during charge and discharge cycles without losing interconnectivity within the electrodes. Interconnectivity of the active ingredients in an electrode is extremely important in battery performance, especially during charging and discharging cycles, as elec-50 trons must move across the electrode, and lithium ion mobility requires interconnectivity within the electrode between particles.

Unfortunately, NMP is a toxic material and presents health and environmental issues. It would be desirable to 55 replace NMP as a solvent for PVDF binders. However, NMP is somewhat unique in its ability to dissolve PVDF that is not nearly as soluble in other organic solvents.

To effectively employ PVDF compositions in electrodeforming processes in organic solvent other than NMP, the 60 PVDF must be dispersed in the diluent. However, the dispersion must be compatible with current manufacturing practices and provide desired properties of the intermediate and final products. Some common criteria include: a) stability of the fluoropolymer dispersion, having sufficient 65 shelf-life, b) stability of the slurry after admixing the electroconductive powders with the dispersion, c) appropriate 2

viscosity of the slurry to facilitate good application properties, and d) sufficient interconnectivity within the electrode.

In addition, after the electrodes are assembled in an electrical storage device, the device should be substantially free of moisture and substantially free of hydrophilic groups that may attract moisture.

Stable PVDF dispersions for use in preparing electrodeforming compositions have now been found for producing high quality electrodes for batteries and other electrical storage devices having interconnectivity.

#### SUMMARY OF THE INVENTION

The present invention provides a slurry composition comprising (a) a binder comprising a polymer comprising a fluoropolymer dispersed in a liquid medium; and (b) at least one conductive carbon material having a BET surface area of greater than  $100~\text{m}^2/\text{g}$ .

The present invention also provides an electrode comprising (a) an electrical current collector; and (b) a film formed on the electrical current collector, wherein the film is deposited from a slurry composition comprising (a) a binder comprising a polymer comprising a fluoropolymer dispersed in a liquid medium; (b) an electrochemically active material; and (c) at least one conductive carbon material having a BET surface area of greater than 100 m<sup>2</sup>/g.

The present invention further provides an electrical storage device comprising (a) an electrode comprising (a) an electrical current collector; and (b) a film formed on the electrical current collector, wherein the film is deposited from a slurry composition comprising (a) a binder comprising a polymer comprising a fluoropolymer dispersed in a liquid medium; (b) an electrochemically active material; and (c) at least one conductive carbon material having a BET surface area of greater than 100 m²/g; (b) a counter electrode; and (c) an electrolyte.

#### DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph illustrating the first derivative of Log viscosity versus temperature, wherein the peak maximum is used to determine the dissolution temperature of PVDF dispersed in 1,2,3-triacetoxypropane (triacetin) from the abscissa.

FIG. 2 is a graph illustrating viscosity as a function of weight percent solids in formulations with high (Triangle) and low (X) surface area carbon for PVDF dissolved in NMP. Results show relative independence of viscosity with carbon type and a limit of roughly 55% solids for a coating application target of 4000 cP.

FIG. 3 is a graph illustrating viscosity as a function of weight percent solids in formulations with high (Triangle) and low (X) surface area carbon for dispersed PVDF binder in triethylphosphate solvent. Results show lower viscosity with high surface area carbon and a limit of roughly 68% solids for a coating application target of 4000 cP.

FIG. 4 is a graph illustrating viscosity as a function of weight percent solids in formulations with high (Triangle) and low (X) surface area carbon for dispersed PVDF binder in triacetin solvent. Results show lower viscosity with high surface area carbon and a limit of roughly 70% solids for a coating application target of 4000 cP.

#### DETAILED DESCRIPTION

The present invention is directed to a slurry composition comprising a binder comprising a polymer comprising a

fluoropolymer dispersed in a liquid medium; and at least one conductive carbon material having a BET surface area of  $100.1~\rm m^2/g$  to  $1000~\rm m^2/g$ . The slurry composition may optionally further comprise a dispersant and/or an electrochemically active material.

According to the present invention, the binder comprises a polymer comprising a fluoropolymer dispersed in liquid medium. The fluoropolymer may serve as all or a component of the binder for the slurry composition.

The fluoropolymer may comprise a (co)polymer comprising the residue of vinylidene fluoride. A non-limiting example of a (co)polymer comprising the residue of vinylidene fluoride is a polyvinylidene fluoride polymer (PVDF). As used herein, the "polyvinylidene fluoride polymer" includes homopolymers, copolymers, such as binary copolymers, and terpolymers, including high molecular weight homopolymers, copolymers, and terpolymers. Such (co)polymers include those containing at least 50 mole percent, such as at least 75 mole %, and at least 80 mole %, 20 and at least 85 mole % of the residue of vinylidene fluoride (also known as vinylidene difluoride). The vinylidene fluoride monomer may be copolymerized with at least one comonomer selected from the group consisting of tetrafluoroethylene, trifluoroethylene, chlorotrifluoroethylene, 25 hexafluoropropene, vinyl fluoride, pentafluoropropene, tetrafluoropropene, perfluoromethyl vinyl ether, perfluoropropyl vinyl ether and any other monomer that would readily copolymerize with vinylidene fluoride in order to produce the fluoropolymer of the present invention. The fluoropoly- 30 mer may also comprise a PVDF homopolymer.

The fluoropolymer may comprise a high molecular weight PVDF having a weight average molecular weight of at least 50,000 g/mol, such as at least 100,000 g/mol, and may range from 50,000 g/mol to 1,500,000 g/mol, such as 100,000 g/mol to 1,000,000 g/mol. PVDF is commercially available, e.g., from Arkema under the trademark KYNAR and from Inner Mongolia 3F Wanhao Fluorochemical Co., Ltd.

The fluoropolymer may comprise a nanoparticle. As used herein, the term "nanoparticle" refers to particles having a 40 particle size of less than 1,000 nm. The fluoropolymer may have a particle size of at least 50 nm, such as at least 100 nm, such as at least 250 nm, such as at least 300 nm, and may be no more than 900 nm, such as no more than 600 nm, such as no more than 450 nm, such as no more than 400 nm, such 45 as no more than 300 nm, such as no more than 200 nm. The fluoropolymer nanoparticles may have a particle size of 50 nm to 900 nm, such as 100 nm to 600 nm, such as 250 nm to 450 nm, such as 300 nm to 400 nm, such as 100 nm to 400 nm, such as 100 nm to 300 nm, such as 100 nm to 200 nm. 50 As used herein, the term "particle size" refers to average diameter of the fluoropolymer particles. The particle size referred to in the present disclosure was determined by the following procedure: A sample was prepared by dispersing the fluoropolymer onto a segment of carbon tape that was 55 attached to an aluminum scanning electron microscope (SEM) stub. Excess particles were blown off the carbon tape with compressed air. The sample was then sputter coated with Au/Pd for 20 seconds and was then analyzed in a Quanta 250 FEG SEM (field emission gun scanning electron 60 microscope) under high vacuum. The accelerating voltage was set to 20.00 kV and the spot size was set to 3.0. Images were collected from three different areas on the prepared sample, and ImageJ software was used to measure the diameter of 10 fluoropolymer particles from each area for a 65 total of 30 particle size measurements that were averaged together to determine the average particle size.

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The fluoropolymer may be present in the binder in amounts of 40% to 100% by weight, such as 40% to 96% by weight, such as 50% to 90% by weight, based on the total weight of the binder solids.

The liquid medium of the slurry composition may comprise an organic medium. As used herein, the term "organic medium" refers to a liquid medium comprising less than 50% by weight water, based on the total weight of the organic medium. Such organic mediums may comprise less than 40% by weight water, or less than 30% by weight water, or less than 20% by weight water, or less than 10% by weight water, or less than 5% by weight water, or less than 1% by weight water, or less than 0.1% by weight water, based on the total weight of the organic medium, or may be free of water. Organic solvent(s) comprise more than 50% by weight of the organic medium, such as at least 70% by weight, such as at least 80% by weight, such as at least 90% by weight, such as at least 95% by weight, such as at least 99% by weight, such as at least 99.9% by weight, such as 100% by weight, based on the total weight of the organic medium. The organic solvent(s) may comprise 50.1% to 100% by weight, such as 70% to 100% by weight, such as 80% to 100% by weight, such as 90% to 100% by weight, such as 95% to 100% by weight, such as 99% to 100% by weight, such as 99.9% to 100% by weight, based on the total weight of the organic medium.

The organic medium may comprise, consist essentially of, or consist of, for example, ketones such as methyl ethyl ketone, cyclohexanone and isophorone, ethers such as the C<sub>1</sub> to C<sub>4</sub> alkyl ethers of ethylene and propylene glycol, butyl pyrrolidone, trialkyl phosphate, 1,2,3-triacetoxypropane, 3-methoxy-N,N-dimethylpropanamide, ethyl acetoacetate, gamma-butyrolactone, propylene glycol methyl ether, propylene carbonate, dimethyl adipate, propylene glycol methyl ether acetate, dibasic ester (DBE), dibasic ester 5 (DBE-5), 4-hydroxy-4-methyl-2-pentanone (diacetone alcohol), propylene glycol diacetate, dimethyl phthalate, methyl isoamyl ketone, ethyl propionate, 1-ethoxy-2-propanol, dipropylene glycol dimethyl ether, saturated and unsaturated linear and cyclic ketones (commercially available as a mixture thereof as Eastman<sup>TM</sup> C-11 Ketone from Eastman Chemical Company), diisobutyl ketone, acetate esters (commercially available as Exxate<sup>TM</sup> 1000 from Hallstar), tripropylene glycol methyl ether, diethylene glycol ethyl ether acetate, or combinations thereof. The trialkyl phosphate may comprise, for example, trimethylphosphate, triethylphosphate, tripropylphosphate, tributylphosphate, or the like.

The organic medium may optionally have an evaporation rate less than 10 g/min m<sup>2</sup>, at the dissolution temperature of the fluoropolymer dispersed in the organic medium. Evaporation rates may be measured using ASTM D3539 (1996). According to the present invention, the dissolution temperature of the fluoropolymer dispersed in the organic medium may be determined by measuring complex viscosity of the mixture as a function of temperature. This technique may be applied to fluoropolymers (in addition to other types of polymers) mixed in an organic medium where the total mass of non-volatile solids content of such mixtures is from 44% to 46%, such as 45% of the total mass of the mixture. Complex viscosity may be measured with an Anton-Paar MCR301 rheometer using a 50-millimeter cone and temperature-controlled plate. The complex viscosity of fluoropolymer mixtures is measured over a temperature range from 35° C. to at least 75° C. with a temperature ramp rate of 10° C. per minute, an oscillatory frequency of 1 Hz, and a stress amplitude limit of 90 Pa. The dissolution of fluoropolymer in the organic medium is indicated by a sharp

increase in the complex viscosity as temperature increased. The dissolution temperature is defined as the temperature at which the rate of change in viscosity with ramping temperature is highest and is calculated by determining the temperature at which the first derivative with respect to temperature of the Log<sub>10</sub> of the complex viscosity reaches a maximum. FIG. 1 is a graph illustrating the first derivative of Log<sub>10</sub> viscosity versus temperature, wherein the peak maximum is used to determine the dissolution temperature of the fluoropolymer polyvinylidene fluoride (PVDF T-1 10 from Inner Mongolia 3F Wanhao Fluorochemical Co. Ltd.) dispersed in the organic medium 1,2,3-triacetoxypropane (triacetin) from the abscissa. The table below illustrates dissolution temperatures determined according to this

method using PVDF T-1 from Inner Mongolia 3F Wanhao 15

Fluorochemical Co. Ltd. (PVDF T-1 has a particle size of

about 330 to 380 nm and a weight average molecular weight

of about 130,000 to 160,000 g/mol), in various solvents or

solvent mixtures as listed.

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3-methoxy-N,N-dimethylpropana-3-triacetoxypropane, mide, ethyl acetoacetate, gamma-butyrolactone, propylene glycol methyl ether, cyclohexanone, propylene carbonate, dimethyl adipate, propylene glycol methyl ether acetate, dibasic ester (DBE), dibasic ester 5 (DBE-5), 4-hydroxy-4methyl-2-pentanone (diacetone alcohol), propylene glycol diacetate, dimethyl phthalate, methyl isoamyl ketone, ethyl propionate, 1-ethoxy-2-propanol, dipropylene glycol dimethyl ether, saturated and unsaturated linear and cyclic ketones (commercially available as a mixture thereof as Eastman<sup>TM</sup> C-11 Ketone from Eastman Chemical Company), diisobutyl ketone, acetate esters (commercially available as Exxate<sup>TM</sup> 1000 from Hallstar), tripropylene glycol methyl ether, diethylene glycol ethyl ether acetate, or combinations thereof. The trialkyl phosphate may comprise, for example, trimethylphosphate, triethylphosphate, tripropylphosphate, tributylphosphate, or the like.

The organic medium may comprise a primary solvent and a co-solvent that form a homogenous continuous phase with

Solvent	Solvent % mass of organic medium	Cosolvent	Cosolvent % mass of organic medium	PVDF % mass of mixture	Dissolution Temp (° C.)	Evaporation rate at Dissolution Temp (g/min m <sup>2</sup> )
N-butylpyrrolidone	100	_	_	45	48	_
gamma-	100	_	_	45	51	9.31
butyrolactone						
Isophorone	100	_	_	45	72	16.59
Triacetin	100	_	_	45	76	0.69
Ethyl Acetoacetate	100	_	_	45	76	37.76
Triethylphosphate	80	Ethyl	20	45	46	_
Triethylphosphate	80	Acetoacetate Dowanol TM PM <sup>1</sup>	20	45	58	_

<sup>1</sup>Propylene glycol methyl ether commercially available from The Dow Chemical Company

The dissolution temperature of the fluoropolymer dispersed in the organic medium may be less than 77° C., such as less than 70° C., such as less than 65° C., such as less than 60° C., such as less than 55° C., such as less than 50° C. The dissolution temperature of the fluoropolymer dispersed in the organic medium may range from 30° C. to 77° C., such as from 30° C. to 70° C., such as 30° C. to 65° C., such as 30° C. to 60° C., such as 30° C. to 55° C., such as 30° C. to 50° C. The dissolution temperature may be measured  $^{45}$  according to the method discussed above.

The organic medium may comprise, for example, butyl pyrrolidone, trialkyl phosphate, 1,2,3-triacetoxypropane, 3-methoxy-N,N-dimethylpropanamide, ethyl acetoacetate, gamma-butyrolactone, propylene glycol methyl ether, 50 cyclohexanone, propylene carbonate, dimethyl adipate, propylene glycol methyl ether acetate, dibasic ester (DBE), dibasic ester 5 (DBE-5), 4-hydroxy-4-methyl-2-pentanone (diacetone alcohol), propylene glycol diacetate, dimethyl phthalate, methyl isoamyl ketone, ethyl propionate, 55 1-ethoxy-2-propanol, dipropylene glycol dimethyl ether, saturated and unsaturated linear and cyclic ketones (commercially available as a mixture thereof as Eastman<sup>™</sup> C-11 Ketone from Eastman Chemical Company), diisobutyl ketone, acetate esters (commercially available as Exxate<sup>TM</sup> 60 1000 from Hallstar), tripropylene glycol methyl ether, diethylene glycol ethyl ether acetate, or combinations thereof. The trialkyl phosphate may comprise, for example, trimethylphosphate, triethylphosphate, tripropylphosphate, tributylphosphate, or the like.

The organic medium may consist essentially of or consist of, for example, butyl pyrrolidone, trialkyl phosphate, 1,2,

the fluoropolymer as the dispersed phase. The primary solvent and co-solvent and relevant amounts thereof may be selected to provide a dispersion of the fluoropolymer in the organic medium at room temperature, i.e., about 23° C. Both the primary solvent and co-solvent may comprise organic solvent(s). The fluoropolymer may be soluble in the primary solvent if used alone but use of the co-solvent with the primary solvent may allow for the fluoropolymer to be stably dispersed in the organic medium. The primary solvent may comprise, consist essentially of, or consist of, for example, butyl pyrrolidone, a trialkylphosphate, 3-methoxy-N,N-dimethylpropanamide, 1,2,3-triacetoxypropane, or combinations thereof. The co-solvent may comprise, consist essentially of, or consist of, for example, ethyl acetoacetate, gamma-butyrolactone, and/or glycol ethers such as propylene glycol methyl ether, dipropylene glycol methyl ether, propylene glycol monopropyl ether, diethylene glycol monobutyl ether, ethylene glycol monohexyl ether, and the like. The primary solvent may be present in an amount of at least 50% by weight, such as at least 65% by weight, such as at least 75 by weight, and may be present in an amount of no more than 99% by weight, such as no more than 90% by weight, such as no more than 85% by weight, based on the total weight of the organic medium. The primary solvent may be present in an amount of 50% to 99% by weight, such as 65% to 90% by weight, such as 75% to 85% by weight, based on the total weight of the organic medium. The co-solvent may be present in an amount of at least 1% by weight, such as at least 10% by weight, such as at least 15% by weight, and may be present in an amount of no more than

50% by weight, such as no more than 35% by weight, such as no more than 25% by weight. The co-solvent may be present in an amount of 1% to 50% by weight, such as 10% to 35% by weight, such as 15% to 25% by weight, based on the total weight of the organic medium.

The organic medium may also have an evaporation rate greater than  $80 \text{ g/min m}^2$ , at  $180^{\circ}$  C., such as greater than  $90 \text{ g/min m}^2$ , at  $180^{\circ}$  C., such as greater than  $100 \text{ g/min m}^2$ , at  $180^{\circ}$  C.

The liquid medium may comprise an aqueous medium. As used herein, the term "aqueous medium" refers to a liquid medium comprising at least 50% by weight water, based on the total weight of the organic medium. Such aqueous mediums may comprise less than 40% by weight organic solvent, or less than 30% by weight organic solvent, or less than 20% by weight organic solvent, or less than 10% by weight organic solvent, or less than 5% by weight organic solvent, or less than 1% by weight organic solvent, or less than 0.1% by weight organic solvent, based on the total 20 weight of the aqueous medium. Water may comprise more than 50% by weight of the aqueous medium, such as at least 60% by weight, such as at least 70% by weight, such as at least 80% by weight, such as at least 90% by weight, such as at least 95% by weight, such as at least 99% by weight, 25 such as at least 99.9% by weight, such as 100% by weight, based on the total weight of the aqueous medium. Water may comprise 50.1% to 100% by weight, such as 70% to 100% by weight, such as 80% to 100% by weight, such as 90% to 100% by weight, such as 95% to 100% by weight, such as 30 99% to 100% by weight, such as 99.9% to 100% by weight, based on the total weight of the aqueous medium.

The liquid medium may be present in an amount of at least 10% by weight, such as at least 15% by weight, such as at least 20% by weight, such as at least 30% by weight, 35 such as at least 35% by weight, such as at least 40% by weight, and may be present in an amount of no more than 80% by weight, such as no more than 70% by weight, such as no more than 60% by weight, such as no more than 50% by weight, such as no more than 45% by weight, such as no 40 more than 45% by weight, such as no more than 40% by weight, such as no more than 35% by weight, such as no more than 29% by weight, such as no more than 25% by weight, based on the total weight of the slurry composition. The liquid medium may be present in an amount of such as 45 20% to 80% by weight, 10% to 70% by weight, such as 30% to 70% by weight, such as 35% to 60% by weight, such as 40% to 50% by weight, 15% to 60% by weight, 15% to 50% by weight, 15% to 45% by weight, 15% to 40% by weight, 15% to 35% by weight, 15% to 29% by weight, 15% to 25% 50 by weight, based on the total weight of the slurry composition.

The slurry composition may be substantially free, essentially free, or completely free of N-Methyl-2-pyrrolidone (NMP). As used herein, the slurry composition is "substantially free" of NMP if NMP is present, if at all, in an amount of less than 5% by weight, based on the total weight of the slurry composition. As used herein, the slurry composition is "essentially free" of NMP if NMP is present, if at all, in an amount of less than 0.3% by weight, based on the total 60 weight of the slurry composition. As used herein, the slurry composition is "completely free" of NMP if NMP is not present in the slurry composition, i.e., 0.0% by weight, based on the total weight of the slurry composition.

The slurry composition may be substantially free, essen-65 tially free, or completely free of ketones such as methyl ethyl ketone, cyclohexanone, isophorone, acetophenone.

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The slurry composition may be substantially free, essentially free, or completely free of ethers such as the  $C_1$  to  $C_4$  alkyl ethers of ethylene or propylene glycol.

The slurry composition further comprises at least one conductive carbon material having a BET surface area of 100.1 m<sup>2</sup>/g to 1000 m<sup>2</sup>/g. As used herein, the term "BET surface area" refers to a specific surface area determined by nitrogen adsorption according to the ASTM D 3663-78 standard based on the Brunauer-Emmett-Teller method described in the periodical "The Journal of the American Chemical Society", 60, 309 (1938). Examples of the conductive carbon materials include any active carbon that have a BET surface area greater than 100 m<sup>2</sup>/g, such as a BET surface area of  $100.1 \text{ m}^2/\text{g}$  to  $1000 \text{ m}^2/\text{g}$ , such as  $150 \text{ m}^2/\text{g}$ to  $600 \text{ m}^2/\text{g}$ , such as  $100.1 \text{ m}^2/\text{g}$  to  $400 \text{ m}^2/\text{g}$ , such as  $200 \text{ m}^2/\text{g}$  $m^2/g$  to  $400 m^2/g$ . In some examples, the conductive carbon may have a BET surface area of about 200 m<sup>2</sup>/g. A suitable conductive carbon material is LITX 200 commercially available from Cabot Corporation. The conductive carbon material can be present in the slurry in amounts of 2% to 20% by weight, such as 5% to 10% by weight based on total solids weight of the slurry.

It has been surprisingly discovered that the use of the present conductive carbon material having a surface area greater than 100 m<sup>2</sup>/g in a battery slurry composition allows for increased solids electrode slurry formulations when compared to a slurry composition using active carbon material having a surface area less than 100 m<sup>2</sup>/g. Additionally, the use of the conductive carbon material having a surface area greater than 100 m<sup>2</sup>/g in a battery slurry composition having a dispersed fluoropolymer also allows for the preparation of a slurry composition having increased solids compared to a slurry composition of PVDF dissolved in an NMP. Further, it was also surprisingly discovered that the use of the present conductive carbon having a surface area greater than 100 m<sup>2</sup>/g in a battery slurry allows a slurry composition comprising the conductive carbon material, the electrochemically active material and binder to have a solids content of 55% and greater and a viscosity below 4,000 cp, as shown in FIGS. 3-4. The use of the present conductive carbon having a surface area greater than 100 m<sup>2</sup>/g in a battery slurry also allows for the preparation of a slurry composition comprising the conductive carbon material, the electrochemically active material and binder to have a solids content of 55% and greater and a viscosity below 5,000 cp, such as a solids content of 55% to 85% by weight, such as 60% to 85% by weight, such as 65% to 85% by weight, such as 71% to 85% by weight, such as 75% to 85% by weight, such as 65% to 75% by weight, such as 68% to 72% by weight, based on the total weight of the slurry composition. The increased solids content in electrode slurries can be desirable because it can allow for reduced manufacturing time, reduced manufacturing costs and increased film thickness when compared with a slurry composition using active carbon materials having a surface area less than 100 m<sup>2</sup>/g and lower solids content.

The slurry composition may optionally further comprise other electrically conductive agents having surface areas of less than 100 m²/g in addition to the conductive carbon material. Non-limiting examples of other electrically conductive agents include carbonaceous materials such as, activated carbon, carbon black such as acetylene black and furnace black, graphite, graphene, carbon nanotubes, carbon fibers, fullerene, and combinations thereof.

Alternatively, the slurry composition may be substantially free, essentially free, or completely free of any or all of the other electrically conductive agents.

The slurry composition may optionally further comprise a dispersant. The dispersant may assist in dispersing the fluoropolymer, and/or, if present, the electrically conductive agent and/or the electrochemically active material in the liquid medium. When present, the dispersant may be a 5 component of the slurry composition binder. The dispersant may comprise at least one phase that is compatible with the fluoropolymer and/or other components of the slurry composition, such as the electrically conductive agent or electrochemically active material, if present, and may further 10 comprise at least one phase that is compatible with the liquid medium. The slurry composition may comprise one, two, three, four or more different dispersants, and each dispersant may assist in dispersing a different component of the slurry composition. The dispersant may comprise any material 15 having phases compatible with both the fluoropolymer and/ or, if present, the electrically conductive agent or electrochemically active material, and the liquid medium. As used herein, the term "compatible" means the ability of a material to form a blend with other materials that is and will remain 20 substantially homogenous over time. The fluoropolymer and dispersant may not be bound by a covalent bond. For example, the dispersant may comprise a polymer comprising such phases. The polymer may be in the form of a block polymer, a random polymer, or a gradient polymer, wherein 25 the phases of present in the different blocks of the polymer, are randomly included throughout the polymer, or are progressively more or less densely present along the polymer backbone, respectively. The dispersant may comprise any suitable polymer to serve this purpose. For example, the 30 polymer may comprise addition polymers produced by polymerizing ethylenically unsaturated monomers, polyepoxide polymers, polyamide polymers, polyurethane polymers, polyurea polymers, polyether polymers, polyacid polymers, and polyester polymers, among others. The dis- 35 persant may also serve as an additional component of the binder of the slurry composition.

The dispersant may comprise functional groups. The functional groups may comprise, for example, active hydrogen functional groups, heterocyclic groups, and combina- 40 tions thereof. As used herein, the term "active hydrogen functional groups" refers to those groups that are reactive with isocyanates as determined by the Zerewitinoff test described in the JOURNAL OF THE AMERICAN CHEMI-CAL SOCIETY, Vol. 49, page 3181 (1927), and include, for 45 example, hydroxyl groups, primary or secondary amino groups, carboxylic acid groups, and thiol groups. As used herein, the term "heterocyclic group" refers to a cyclic group containing at least two different elements in its ring such as a cyclic moiety having at least one atom in addition to 50 carbon in the ring structure, such as, for example, oxygen, nitrogen or sulfur. Non-limiting examples of heterocylic groups include epoxides, lactams and lactones. In addition, when epoxide functional groups are present on the addition polymer, the epoxide functional groups on the dispersant 55 may be post-reacted with a beta-hydroxy functional acid. Non-limiting examples of beta-hydroxy functional acids include citric acid, tartaric acid, and/or an aromatic acid, such as 3-hydroxy-2-naphthoic acid. The ring opening reaction of the epoxide functional group will yield hydroxyl 60 functional groups on the dispersant.

When acid functional groups are present, the dispersant may have a theoretical acid equivalent weight of at least 350 g/acid equivalent, such as at least 878 g/acid equivalent, such as at least 1,757 g/acid equivalent, and may be no more 65 than 17,570 g/acid equivalent, such as no more than 12,000 g/acid equivalent, such as no more than 7,000 g/acid equivalent.

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lent. The dispersant may have a theoretical acid equivalent weight of 350 to 17,570 g/acid equivalent, such as 878 to 12,000 g/acid equivalent, such as 1,757 to 7,000 g/acid equivalent.

As mentioned above, the dispersant may comprise an addition polymer. The addition polymer may be derived from, and comprise constitutional units comprising the residue of, one or more alpha, beta-ethylenically unsaturated monomers, such as those discussed below, and may be prepared by polymerizing a reaction mixture of such monomers. The mixture of monomers may comprise one or more active hydrogen group-containing ethylenically unsaturated monomers. The reaction mixture may also comprise ethylenically unsaturated monomers comprising a heterocyclic group. As used herein, an ethylenically unsaturated monomer comprising a heterocyclic group refers to a monomer having at least one alpha, beta ethylenic unsaturated group and at least cyclic moiety having at least one atom in addition to carbon in the ring structure, such as, for example, oxygen, nitrogen or sulfur. Non-limiting examples of ethylenically unsaturated monomers comprising a heterocyclic group include epoxy functional ethylenically unsaturated monomers, vinyl pyrrolidone and vinyl caprolactam, among others. The reaction mixture may additionally comprise other ethylenically unsaturated monomers such as alkyl esters of (meth)acrylic acid and others described below.

The addition polymer may comprise a (meth)acrylic polymer that comprises constitutional units comprising the residue of one or more (meth)acrylic monomers. The (meth) acrylic polymer may be prepared by polymerizing a reaction mixture of alpha, beta-ethylenically unsaturated monomers that comprise one or more (meth)acrylic monomers and optionally other ethylenically unsaturated monomers. As used herein, the term "(meth)acrylic monomer" refers to acrylic acid, methacrylic acid, and monomers derived therefrom, including alkyl esters of acrylic acid and methacrylic acid, and the like. As used herein, the term "(meth)acrylic polymer" refers to a polymer derived from or comprising constitutional units comprising the residue of one or more (meth)acrylic monomers. The mixture of monomers may comprise one or more active hydrogen group-containing (meth)acrylic monomers, ethylenically unsaturated monomers comprising a heterocyclic group, and other ethylenically unsaturated monomers. The (meth)acrylic polymer may also be prepared with an epoxy functional ethylenically unsaturated monomer such as glycidyl methacrylate in the reaction mixture, and epoxy functional groups on the resulting polymer may be post-reacted with a beta-hydroxy functional acid such as citric acid, tartaric acid, and/or 3-hydroxy-2-naphthoic acid to yield hydroxyl functional groups on the (meth)acrylic polymer.

The addition polymer may comprise constitutional units comprising the residue of an alpha, beta-ethylenically unsaturated carboxylic acid. Non-limiting examples of alpha, beta-ethylenically unsaturated carboxylic acids include those containing up to 10 carbon atoms such as acrylic acid and methacrylic acid. Non-limiting examples of other unsaturated acids are alpha, beta-ethylenically unsaturated dicarboxylic acids such as maleic acid or its anhydride, fumaric acid and itaconic acid. Also, the half esters of these dicarboxylic acids may be employed. The constitutional units comprising the residue of the alpha, beta-ethylenically unsaturated carboxylic acids may comprise at least 1% by weight, such as at least 2% by weight, such as at least 5% by weight, and may be no more than 50% by weight, such as no more than 20% by weight, such as no more than 10% by weight, such as no more than 5% by weight, based on the

total weight of the addition polymer. The constitutional units comprising the residue of the alpha, beta-ethylenically unsaturated carboxylic acids may comprise 1% to 50% by weight, 2% to 50% by weight, such as 2% to 20% by weight, such as 2% to 10% by weight, such as 2% to 5% by weight, 5 such as 1% to 5% by weight, based on the total weight of the addition polymer. The addition polymer may be derived from a reaction mixture comprising the alpha, beta-ethylenically unsaturated carboxylic acids in an amount of 1% to 50% by weight, 2% to 50% by weight, such as 2% to 20% 10 by weight, such as 2% to 10% by weight, such as 2% to 5% by weight, such as 1% to 5% by weight, based on the total weight of polymerizable monomers used in the reaction mixture. The inclusion of constitutional units comprising the residue of an alpha, beta-ethylenically unsaturated carbox- 15 ylic acids in the dispersant results in a dispersant comprising at least one carboxylic acid group which may assist in providing stability to the dispersion.

The addition polymer may comprise constitutional units comprising the residue of an alkyl esters of (meth)acrylic 20 acid containing from 1 to 3 carbon atoms in the alkyl group. Non-limiting examples of alkyl esters of (meth)acrylic acid containing from 1 to 3 carbon atoms in the alkyl group include methyl (meth)acrylate and ethyl (meth)acrylate. The constitutional units comprising the residue of the alkyl esters 25 of (meth)acrylic acid containing from 1 to 3 carbon atoms in the alkyl group may comprise at least 20% by weight, such as at least 30% by weight, such as at least 40% by weight, such as at least 45% by weight, such as at least 50% by weight, and may be no more than 98% by weight, such as no more than 96% by weight, such as no more than 90% by weight, such as no more than 80% by weight, such as no more than 75% by weight, based on the total weight of the addition polymer. The constitutional units comprising the residue of the alkyl esters of (meth)acrylic acid containing 35 from 1 to 3 carbon atoms in the alkyl group may comprise 20% to 98% by weight, such as 30% to 96% by weight, such as 30% to 90% by weight, 40% to 90% by weight, such as 40% to 80% by weight, such as 45% to 75% by weight, based on the total weight of the addition polymer. The 40 addition polymer may be derived from a reaction mixture comprising the alkyl esters of (meth)acrylic acid containing from 1 to 3 carbon atoms in the alkyl group in an amount of 20% to 98% by weight, such as 30% to 96% by weight, such as 30% to 90% by weight, 40% to 90% by weight, such as 45 40% to 80% by weight, such as 45% to 75% by weight, based on the total weight of polymerizable monomers used in the reaction mixture.

The addition polymer may comprise constitutional units comprising the residue of an alkyl esters of (meth)acrylic 50 acid containing from 4 to 18 carbon atoms in the alkyl group. Non-limiting examples of alkyl esters of (meth)acrylic acid containing from 4 to 18 carbon atoms in the alkyl group include butyl (meth)acrylate, hexyl (meth)acrylate, octyl (meth)acrylate, isodecyl (meth)acrylate, stearyl (meth)acry- 55 late, 2-ethylhexyl (meth)acrylate, decyl (meth)acrylate and dodecyl (meth)acrylate. The constitutional units comprising the residue of the alkyl esters of (meth)acrylic acid containing from 4 to 18 carbon atoms in the alkyl group may comprise at least 2% by weight, such as at least 5% by 60 weight, such as at least 10% by weight, such as at least 15% by weight, such as at least 20% by weight, and may be no more than 70% by weight, such as no more than 60% by weight, such as no more than 50% by weight, such as no more than 40% by weight, such as no more than 35% by 65 weight, based on the total weight of the addition polymer. The constitutional units comprising the residue of the alkyl

esters of (meth)acrylic acid containing from 4 to 18 carbon atoms in the alkyl group may comprise 2% to 70% by weight, such as 2% to 60% by weight, such as 5% to 50% by weight, 10% to 40% by weight, such as 15% to 35% by weight, based on the total weight of the addition polymer. The addition polymer may be derived from a reaction mixture comprising the alkyl esters of (meth)acrylic acid containing from 4 to 18 carbon atoms in the alkyl group in an amount of 2% to 70% by weight, such as 2% to 60% by weight, such as 5% to 50% by weight, 10% to 40% by weight, such as 15% to 35% by weight, based on the total weight of polymerizable monomers used in the reaction mixture.

The addition polymer may comprise constitutional units comprising the residue of a hydroxyalkyl ester. Non-limiting examples of hydroxyalkyl esters include hydroxyethyl (meth)acrylate and hydroxypropyl (meth)acrylate. The constitutional units comprising the residue of the hydroxyalkyl ester may comprise at least 0.5% by weight, such as at least 1% by weight, such as at least 2% by weight, and may be no more than 30% by weight, such as no more than 20% by weight, such as no more than 10% by weight, such as no more than 5% by weight, based on the total weight of the addition polymer. The constitutional units comprising the residue of the hydroxyalkyl ester may comprise 0.5% to 30% by weight, such as 1% to 20% by weight, such as 2% to 20% by weight, 2% to 10% by weight, such as 2% to 5% by weight, based on the total weight of the addition polymer. The addition polymer may be derived from a reaction mixture comprising the hydroxyalkyl ester in an amount of 0.5% to 30% by weight, such as 1% to 20% by weight, such as 2% to 20% by weight, 2% to 10% by weight, such as 2% to 5% by weight, based on the total weight of polymerizable monomers used in the reaction mixture. The inclusion of constitutional units comprising the residue of a hydroxyalkyl ester in the dispersant results in a dispersant comprising at least one hydroxyl group (although hydroxyl groups may be included by other methods). Hydroxyl groups resulting from inclusion of the hydroxyalkyl esters (or incorporated by other means) may react with a separately added crosslinking agent that comprises functional groups reactive with hydroxyl groups such as, for example, an aminoplast, phenolplast, polyepoxides and blocked polyisocyanates, or with N-alkoxymethyl amide groups or blocked isocyanato groups present in the addition polymer when self-crosslinking monomers that have groups that are reactive with the hydroxyl groups are incorporated into the addition polymer.

The addition polymer may comprise constitutional units comprising the residue of an ethylenically unsaturated monomer comprising a heterocyclic group. Non-limiting examples of ethylenically unsaturated monomers comprising a heterocyclic group include epoxy functional ethylenically unsaturated monomers, such as glycidyl (meth)acrylate, vinyl pyrrolidone and vinyl caprolactam, among others. The constitutional units comprising the residue of the ethylenically unsaturated monomers comprising a heterocyclic group may comprise at least 0.5% by weight, such as at least 1% by weight, such as at least 5% by weight, such as at least 8% by weight, and may be no more than 99% by weight, such as no more than 50% by weight, such as no more than 40% by weight, such as no more than 30% by weight, such as no more than 27% by weight, based on the total weight of the addition polymer. The constitutional units comprising the residue of the ethylenically unsaturated monomers comprising a heterocyclic group may comprise 0.5% to 99% by weight, such as 0.5% to 50% by weight, such as 1% to 40% by weight, such as 5% to 30% by weight, 8% to 27% by

weight, based on the total weight of the addition polymer. The addition polymer may be derived from a reaction mixture comprising the ethylenically unsaturated monomers comprising a heterocyclic group in an amount of 0.5% to 50% by weight, such as 1% to 40% by weight, such as 5% 5 to 30% by weight, 8% to 27% by weight, based on the total weight of polymerizable monomers used in the reaction mixture.

As noted above, the addition polymer may comprise constitutional units comprising the residue of a self-crosslinking monomer, and the addition polymer may comprise a self-crosslinking addition polymer. As used herein, the term "self-crosslinking monomer" refers to monomers that incorporate functional groups that may react with other functional groups present on the dispersant to a crosslink between the 15 dispersant or more than one dispersant. Non-limiting examples of self-crosslinking monomers include N-alkoxymethyl (meth)acrylamide monomers such as N-butoxymethyl (meth)acrylamide and N-isopropoxymethyl (meth)acrylamide, as well as self-crosslinking monomers 20 containing blocked isocyanate groups, such as isocyanatoethyl (meth)acrylate in which the isocyanato group is reacted ("blocked") with a compound that unblocks at curing temperature. Examples of suitable blocking agents include epsilon-caprolactone and methylethyl ketoxime. The 25 constitutional units comprising the residue of the selfcrosslinking monomer may comprise at least 0.5% by weight, such as at least 1% by weight, such as at least 2% by weight, and may be no more than 30% by weight, such as no more than 20% by weight, such as no more than 10% 30 by weight, such as no more than 5% by weight, based on the total weight of the addition polymer. The constitutional units comprising the residue of the self-crosslinking monomer may comprise 0.5% to 30% by weight, such as 1% to 20% by weight, such as 2% to 20% by weight, 2% to 10% by 35 weight, such as 2% to 5% by weight, based on the total weight of the addition polymer. The addition polymer may be derived from a reaction mixture comprising the selfcrosslinking monomer in an amount of 0.5% to 30% by weight, such as 1% to 20% by weight, such as 2% to 20% 40 by weight, 2% to 10% by weight, such as 2% to 5% by weight, based on the total weight of polymerizable monomers used in the reaction mixture.

The addition polymer may comprise constitutional units comprising the residue of other alpha, beta-ethylenically 45 unsaturated monomers. Non-limiting examples of other alpha, beta-ethylenically unsaturated monomers include vinyl aromatic compounds such as styrene, alpha-methyl styrene, alpha-chlorostyrene and vinyl toluene; organic nitriles such as acrylonitrile and methacrylonitrile; allyl 50 monomers such as allyl chloride; allyl cyanide and monomeric dienes such as 1,3-butadiene and 2-methyl-1,3-butadiene; and acetoacetoxyalkyl (meth)acrylates such as acetoacetoxyethyl methacrylate (AAEM) (which may be self-crosslinking). The constitutional units comprising the 55 residue of the other alpha, beta-ethylenically unsaturated monomers may comprise at least 0.5% by weight, such as at least 1% by weight, such as at least 2% by weight, and may be no more than 30% by weight, such as no more than 20% by weight, such as no more than 10% by weight, such as no 60 more than 5% by weight, based on the total weight of the addition polymer. The constitutional units comprising the residue of the other alpha, beta-ethylenically unsaturated monomers may comprise 0.5% to 30% by weight, such as 1% to 20% by weight, such as 2% to 20% by weight, 2% to 65 10% by weight, such as 2% to 5% by weight, based on the total weight of the addition polymer. The addition polymer

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may be derived from a reaction mixture comprising the other alpha, beta-ethylenically unsaturated monomers in an amount of 0.5% to 30% by weight, such as 1% to 20% by weight, such as 2% to 20% by weight, 2% to 10% by weight, such as 2% to 5% by weight, based on the total weight of polymerizable monomers used in the reaction mixture.

The monomers and relative amounts may be selected such that the resulting addition polymer has a Tg of 100° C. or less, typically from -50° C. to +70° C., such as -50° C. to 0° C. A lower Tg that is below 0° C. may be desirable to ensure acceptable battery performance at low temperatures.

The addition polymers may be prepared by conventional free radical initiated solution polymerization techniques in which the polymerizable monomers are dissolved in a second organic medium comprising a solvent or a mixture of solvents and polymerized in the presence of a free radical initiator until conversion is complete. The second organic medium used to prepare the addition polymer may be the same as the organic medium present in the slurry composition such that the composition of the organic medium is unchanged by addition of the addition polymer solution. For example, the second organic medium may comprise the same primary solvent(s) and co-solvent(s) in the same ratios as the organic medium of the slurry composition. Alternatively, the second organic medium used to prepare the addition polymer may be different and distinct from the organic medium of the slurry composition. The second organic medium used to produce the addition polymer may comprise any suitable organic solvent or mixture of solvents, including those discussed above with respect to the organic medium, such as, for example, triethylphosphate.

Examples of free radical initiators are those which are soluble in the mixture of monomers such as azobisisobuty-ronitrile, azobis(alpha, gamma-methylvaleronitrile), tertiary-butyl perbenzoate, tertiary-butyl peracetate, benzoyl peroxide, ditertiary-butyl peroxide and tertiary amyl peroxy 2-ethylhexyl carbonate.

Optionally, a chain transfer agent which is soluble in the mixture of monomers such as alkyl mercaptans, for example, tertiary-dodecyl mercaptan; ketones such as methyl ethyl ketone, chlorohydrocarbons such as chloroform can be used. A chain transfer agent provides control over the molecular weight to give products having required viscosity for various coating applications. Tertiary-dodecyl mercaptan is preferred because it results in high conversion of monomer to polymeric product.

To prepare the addition polymer, the solvent may be first heated to reflux and the mixture of polymerizable monomers containing the free radical initiator may be added slowly to the refluxing solvent. The reaction mixture is then held at polymerizing temperatures so as to reduce the free monomer content, such as to below 1.0 percent and usually below 0.5 percent, based on the total weight of the mixture of polymerizable monomers.

For use in the slurry composition of the invention, the dispersants prepared as described above usually have a weight average molecular weight of about 5000 to 500,000 g/mol, such as 10,000 to 100,000 g/mol, and 25,000 to 50,000 g/mol.

The dispersant may be present in the binder in amounts of 2% to 20% by weight, such as 5% to 15% by weight, based on the total weight of the binder solids.

As noted above, the slurry composition may optionally further comprise a separately added crosslinking agent for reaction with the dispersant. The crosslinking agent should be soluble or dispersible in the organic medium and be reactive with active hydrogen groups of the dispersant, such

as the carboxylic acid groups and the hydroxyl groups, if present. Non-limiting examples of suitable crosslinking agents include aminoplast resins, blocked polyisocyanates and polyepoxides.

Examples of aminoplast resins for use as a crossslinking agent are those which are formed by reacting a triazine such as melamine or benzoguanamine with formaldehyde. These reaction products contain reactive N-methylol groups. Usually, these reactive groups are etherified with methanol, ethanol, butanol including mixtures thereof to moderate their reactivity. For the chemistry preparation and use of aminoplast resins, see "The Chemistry and Applications of Amino Crosslinking Agents or Aminoplast", Vol. V, Part II, page 21 ff., edited by Dr. Oldring; John Wiley & Sons/Cita Technology Limited, London, 1998. These resins are commercially available under the trademark MAPRENAL® such as MAPRENAL MF980 and under the trademark CYMEL® such as CYMEL 303 and CYMEL 1128, available from Cytec Industries.

Blocked polyisocyanate crosslinking agents are typically diisocyanates such as toluene diisocyanate, 1,6-hexamethylene diisocyanate and isophorone diisocyanate including isocyanato dimers and trimers thereof in which the isocyanate groups are reacted ("blocked") with a material such as 25 epsilon-caprolactone and methylethyl ketoxime. At curing temperatures, the blocking agents unblock exposing isocyanate functionality that is reactive with the hydroxyl functionality associated with the (meth)acrylic polymer. Blocked polyisocyanate crosslinking agents are commercially available from Covestro as DESMODUR BL.

Examples of polyepoxide crosslinking agents are epoxycontaining (meth)acrylic polymers such as those prepared from glycidyl methacrylate copolymerized with other vinyl monomers, polyglycidyl ethers of polyhydric phenols such 35 as the diglycidyl ether of bisphenol A; and cycloaliphatic polyepoxides such as 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate and bis(3,4-epoxy-6-methylcyclohexyl-methyl) adipate.

In addition to promoting the cross-linking of the dispersant, the crosslinking agents, including those associated with crosslinking monomers and separately added crosslinking agents, react with the hydrophilic groups, such as active hydrogen functional groups of the dispersant preventing these groups from absorbing moisture that could be problematic in a lithium ion battery.

The separately added crosslinker may be present in the binder in amounts of up to 15% by weight, such as 1% to 15% by weight, the % by weight being based on the total weight of the binder solids.

The slurry composition may optionally further comprise an adhesion promoter. The adhesion promoter may comprise a polyvinylidene fluoride copolymer different than the fluoropolymer described above, an acid-functional polyolefin, or a thermoplastic material.

The polyvinylidene fluoride copolymer adhesion promoter comprises constitutional units comprising the residue of vinylidene fluoride and at least one of (i) a (meth)acrylic acid; and/or (ii) a hydroxyalkyl (meth)acrylate. The (meth) acrylic acid may comprise acrylic acid, methacrylic acid, or 60 combinations thereof. The hydroxyalkyl (meth)acrylate may comprise a C<sub>1</sub> to C<sub>5</sub> hydroxyalkyl (meth)acrylate, such as, for example, hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, or combinations thereof. A commercially available example of such an 65 addition polymer includes SOLEF 5130, available from Solvay. Unlike the fluoropolymer discussed above, the poly-

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vinylidene fluoride copolymer may be dispersed or solubilized in the organic medium of the slurry composition.

The acid-functional polyolefin adhesion promoter comprises an ethylene-(meth)acrylic acid copolymer, such as an ethylene-acrylic acid copolymer or an ethylene-methacrylic acid copolymer. The ethylene-acrylic acid copolymer may comprise constitutional units comprising 10% to 50% by weight acrylic acid, such as 15% to 30% by weight, such as 17% to 25% by weight, such as about 20% by weight, based on the total weight of the ethylene-acrylic acid copolymer, and 50% to 90% by weight ethylene, such as 70% to 85% by weight, such as 75% to 83% by weight, such as about 80% by weight, based on the total weight of the ethylene-acrylic acid copolymer. A commercially available example of such an addition polymer includes PRIMACOR 5980i, available from the Dow Chemical Company.

The adhesion promoter may be present in the slurry composition in an amount of 10% to 60% by weight, 20% to 60% by weight, such as 30% to 60% by weight, such as 20 10% to 50% by weight, such as 15% to 40% by weight, such as 20% to 30% by weight, such as 35% to 35% by weight, based on the total weight of the binder solids.

The binder typically has a resin solids content of from 30% to 80% by weight, such as 40% to 70% by weight, based on the total weight of the binder dispersion. As used herein, the term "resin solids" may be used synonymously with "binder solids" and include the fluoropolymer and, if present, the dispersant, adhesion promoter, and separately added crosslinking agent. As used herein, the term "binder dispersion" refers to a dispersion of the binder solids in the liquid medium. The fluoropolymer may be present in in the binder in amounts of 45% to 96% by weight, such as 50% to 90% by weight; the dispersant may be present in amounts of 2% to 20% by weight, such as 5% to 15% by weight; the adhesion promoter may be present in the slurry composition in an amount of 10% to 60% by weight, 20% to 60% by weight, such as 30% to 60% by weight, such as 10% to 50% by weight, such as 15% to 40% by weight, such as 20% to 30% by weight, such as 35% to 35% by weight; and the separately added crosslinker may be present in amounts of up to 15% by weight, such as 1% to 15% by weight, the % by weight being based on the total weight of the binder solids. The liquid medium is present in the binder dispersion in amounts of 20% to 80% by weight, such as 20% to 70% by weight, such as 30% to 70% by weight, such as 30% to 60% by weight, based on total weight of the binder dispersion. The binder dispersion may be prepared by adding the fluoropolymer to the liquid medium optionally containing the dispersant and the crosslinking agent, if present, with 50 low shear mixing until a stable dispersion is formed.

The binder solids may be present in the slurry in amounts of 1% to 20% by weight, such as 1% to 10% by weight, such as 5% to 10% percent by weight, based on the total solids weight of the slurry.

The slurry composition may optionally further comprise an electrochemically active material. The material constituting the electrochemically active material contained in the slurry is not particularly limited and a suitable material can be selected according to the type of an electrical storage device of interest.

The electrochemically active material may comprise a material for use as an active material for a positive electrode. The electrochemically active material may comprise a material capable of incorporating lithium (including incorporation through lithium intercalation/deintercalation), a material capable of lithium conversion, or combinations thereof. Non-limiting examples of electrochemically active materials

capable of incorporating lithium include LiCoO<sub>2</sub>, LiNiO<sub>2</sub>, LiFePO<sub>4</sub>, LiCoPO<sub>4</sub>, LiMnO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, Li(NiMnCo)O<sub>2</sub>, Li(NiCoAl)O<sub>2</sub>, carbon-coated LiFePO<sub>4</sub>, and combinations thereof. Non-limiting examples of materials capable of lithium conversion include sulfur, LiO<sub>2</sub>, FeF<sub>2</sub> and FeF<sub>3</sub>, Si, 5 aluminum, tin, SnCo, Fe<sub>3</sub>O<sub>4</sub>, and combinations thereof.

The electrochemically active material may comprise a material for use as an active material for a negative electrode. The electrochemically active material may comprise graphite, lithium titanate, silicon compounds, tin, tin compounds, sulfur, sulfur compounds, or a combination thereof.

The electrochemically active material may be present in the slurry in amounts of 45% to 95% by weight, such as 50% to 90% by weight, such as 70% to 98% by weight, based on the total solids weight of the slurry.

The slurry composition may be in the form of an electrode slurry composition comprising the binder, electrochemically active material and at least one conductive carbon material having a surface area of 100.1 m<sup>2</sup>/g to 1000 m<sup>2</sup>/g, each as described above. The electrode slurry may comprise such 20 materials present in the slurry composition in the amounts described above. For example, the electrode slurry composition may comprise the electrochemically active material present in amounts of 45% to 95% by weight, such as 70% 20% by weight, such as 2% to 20% by weight, such as 1% to 10% by weight, such as 5% to 10% percent by weight; and the electrically conductive agent present in amounts of 1% to 20% by weight, such as 5% to 10% by weight, the percentages by weight based on the total solids weight of the 30 electrode slurry composition.

The electrode slurry composition comprising the liquid medium, electrochemically active material, conductive carbon material having a surface area of greater than 100 m<sup>2</sup>/g, binder dispersion (which may include a separately added 35 crosslinking agent), additional liquid medium, if needed, and optional ingredients, may be prepared by combining the ingredients to form the slurry. These substances can be mixed together by agitation with a known means such as a stirrer, bead mill or high-pressure homogenizer.

As for mixing and agitation for the manufacture of the electrode slurry composition, a mixer capable of stirring these components to such an extent that satisfactory dispersion conditions are met should be selected. The degree of dispersion can be measured with a particle gauge and mixing 45 and dispersion are preferably carried out to ensure that agglomerates of 100 microns or more are not present. Examples of the mixers which meet this condition include ball mill, sand mill, pigment disperser, grinding machine, extruder, rotor stator, pug mill, ultrasonic disperser, homog- 50 enizer, planetary mixer, Hobart mixer, and combinations thereof.

The slurry composition may have a solids content of at least 10% by weight, such as 20% by weight, such as at least 30% by weight, such as at least 40% by weight, such as at 55 least 50% by weight, such as at least 55%, such as at least 60%, such as at least 65%, such as at least 71%, such as at least 75%, and may be no more than 90% by weight, such as no more than 85%, such as no more than 70% by weight, such as no more than 65% by weight, such as no more than 60 60% by weight, the % by weight based on the total weight of the slurry composition. The slurry composition may have a solids content of 10% to 90% by weight, 20% to 60% by weight, such as 30% to 70% by weight, such as 40% to 65% by weight, such as 50% to 60% by weight, such as 30% to 65 90% by weight, such as 40% to 85% by weight, such as 50% to 85% by weight, such as 55% to 85% by weight, such as

60% to 85% by weight, such as 65% to 85% by weight, such as 71% to 85% by weight, such as 75% to 85% by weight, based on the total weight of the slurry composition.

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The present invention is also directed to an electrode comprising an electrical current collector and a film formed on the electrical current collector, wherein the film is deposited from the electrode slurry composition described above. The electrode may be a positive electrode or a negative electrode and may be manufactured by applying the abovedescribed slurry composition to the surface of the current collector to form a coating film, and subsequently drying and/or curing the coating film. The coating film may comprise a cross-linked coating. The current collector may comprise a conductive material, and the conductive material may comprise a metal such as iron, copper, aluminum, nickel, and alloys thereof, as well as stainless steel. For example, the current collector may comprise aluminum or copper in the form of a mesh, sheet or foil. Although the shape and thickness of the current collector are not particularly limited, the current collector may have a thickness of about 0.001 to 0.5 mm, such as a mesh, sheet or foil having a thickness of about 0.001 to 0.5 mm.

In addition, the current collector may be pretreated with to 98% by weight; the binder present in amounts of 1% to 25 a pretreatment composition prior to depositing the slurry composition. As used herein, the term "pretreatment composition" refers to a composition that upon contact with the current collector, reacts with and chemically alters the current collector surface and binds to it to form a protective layer. The pretreatment composition may be a pretreatment composition comprising a group IIIB and/or IVB metal. As used herein, the term "group IIIB and/or IVB metal" refers to an element that is in group IIIB or group IVB of the CAS Periodic Table of the Elements as is shown, for example, in the Handbook of Chemistry and Physics, 63rd edition (1983). Where applicable, the metal themselves may be used, however, a group IIIB and/or IVB metal compound may also be used. As used herein, the term "group IIIB and/or IVB metal compound" refers to compounds that 40 include at least one element that is in group IIIB or group IVB of the CAS Periodic Table of the Elements. Suitable pretreatment compositions and methods for pretreating the current collector are described in U.S. Pat. No. 9,273,399 at col. 4, line 60 to col. 10, line 26, the cited portion of which is incorporated herein by reference. The pretreatment composition may be used to treat current collectors used to produce positive electrodes or negative electrodes.

> To prepare an electrode for a lithium ion electrical storage device, an electrode slurry composition comprising the organic medium, electrochemically active material, electrically conductive agent, binder dispersion (which may include a separately added crosslinking agent), additional organic medium, if needed, and optional ingredients, is prepared by combining the ingredients to form the slurry. These substances can be mixed together by agitation with a known means such as a stirrer, bead mill or high-pressure homogenizer.

> The method of applying the slurry composition to the current collector is not particularly limited. The slurry composition may be applied by doctor blade coating, dip coating, reverse roll coating, direct roll coating, gravure coating, extrusion coating, immersion or brushing. Although the application quantity of the slurry composition is not particularly limited, the thickness of the coating formed after the organic medium is removed may be at least 1 micron, such as 1 to 500 microns (μm), such as 1 to 150 μm, such as 25 to 150  $\mu m$ , such as 30 to 125  $\mu m$ .

Drying and/or crosslinking the coating film after application, if applicable, can be done, for example, by heating at elevated temperature, such as at least 50° C., such as at least 60° C., such as 50-145° C., such as 60-120° C., such as 65-110° C. The time of heating will depend somewhat on the temperature. Generally, higher temperatures require less time for curing. Typically, curing times are at least 5 minutes, such as 5 to 60 minutes. The temperature and time should be sufficient such that the dispersant in the cured film is crosslinked (if applicable), that is, covalent bonds are formed between co-reactive groups on the dispersant polymer chain, such as carboxylic acid groups and hydroxyl groups and the N-methylol and/or the N-methylol ether groups of an aminoplast, isocyanato groups of a blocked polyisocyanate crosslinking agent, or in the case of a selfcuring dispersant, the N-alkoxymethyl amide groups or blocked isocyanato groups. The extent of cure or crosslinking may be measured as resistance to solvents such as methyl ethyl ketone (MEK). The test is performed as 20 described in ASTM D-540293. The number of double rubs, one back and forth motion, is reported. This test is often referred to as "MEK Resistance". Accordingly, the dispersant and crosslinking agent (inclusive of self-curing dispersants and dispersants with separately added crosslinking 25 agents) is isolated from the binder composition, deposited as a film and heated for the temperature and time that the binder film is heated. The film is then measured for MEK Resistance with the number of double rubs reported. Accordingly, a crosslinked dispersant will have an MEK Resistance of at 30 least 50 double rubs, such as at least 75 double rubs. Also, the crosslinked dispersant may be substantially solvent resistant to the solvents of the electrolyte mentioned below. Other methods of drying the coating film include ambient temperature drying, microwave drying and infrared drying, 35 and other methods of curing the coating film include e-beam curing and UV curing.

During discharge of a lithium ion electrical storage device, lithium ions may be released from the negative electrode and carry the current to the positive electrode. This 40 process may include the process known as deintercalation. During charging, the lithium ions migrate from the electrochemically active material in the positive electrode to the negative electrode where they become embedded in the electrochemically active material present in the negative 45 electrode. This process may include the process known as intercalation.

The present invention is also directed to an electrical storage device. An electrical storage device according to the present invention can be manufactured by using the above 50 electrodes prepared from the electrode slurry composition of the present invention. The electrical storage device comprises an electrode, a counter electrode and an electrolyte. The electrode, counter-electrode or both may comprise the electrode of the present invention, as long as one electrode is a positive electrode and one electrode is a negative electrode. Electrical storage devices according to the present invention include a cell, a battery, a battery pack, a secondary battery, a capacitor, and a supercapacitor.

The electrical storage device includes an electrolytic 60 solution and can be manufactured by using parts such as a separator in accordance with a commonly used method. As a more specific manufacturing method, a negative electrode and a positive electrode are assembled together with a separator there between, the resulting assembly is rolled or 65 bent in accordance with the shape of a battery and put into a battery container, an electrolytic solution is injected into

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the battery container, and the battery container is sealed up. The shape of the battery may be like a coin, button or sheet, cylindrical, square or flat.

The electrolytic solution may be liquid or gel, and an electrolytic solution which can serve effectively as a battery may be selected from among known electrolytic solutions which are used in electrical storage devices in accordance with the types of a negative electrode active material and a positive electrode active material. The electrolytic solution may be a solution containing an electrolyte dissolved in a suitable solvent. The electrolyte may be conventionally known lithium salt for lithium ion secondary batteries. Examples of the lithium salt include LiClO<sub>4</sub>, LiBF<sub>4</sub>, LiPF<sub>6</sub>,  $\mathrm{LiCF_3CO_2},\ \mathrm{LiAsF_6},\ \mathrm{LiSbF_6},\ \mathrm{LiB_{10}Cl_{10}},\ \mathrm{LiAlCl_4},\ \mathrm{LiCl},$ LiBr, LiB( $C_2H_5$ )<sub>4</sub>, LiB( $C_6H_5$ )<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, LiCH<sub>3</sub>SO<sub>3</sub>, LiC<sub>4</sub>F<sub>9</sub>SO<sub>3</sub>, Li(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N, LiB<sub>4</sub>CH<sub>3</sub>SO<sub>3</sub>Li and CF<sub>3</sub>SO<sub>3</sub>Li. The solvent for dissolving the above electrolyte is not particularly limited and examples thereof include carbonate compounds such as propylene carbonate, ethylene carbonate, butylene carbonate, dimethyl carbonate, methyl ethyl carbonate and diethyl carbonate; lactone compounds such as γ-butyl lactone; ether compounds such as trimethoxymethane, 1,2-dimethoxyethane, diethyl ether, 2-ethoxyethane, tetrahydrofuran and 2-methyltetrahydrofuran; and sulfoxide compounds such as dimethyl sulfoxide. The concentration of the electrolyte in the electrolytic solution may be 0.5 to 3.0 mole/L, such as 0.7 to 2.0 mole/L.

As used herein, the term "polymer" refers broadly to oligomers and both homopolymers and copolymers. The term "resin" is used interchangeably with "polymer".

The terms "acrylic" and "acrylate" are used interchangeably (unless to do so would alter the intended meaning) and include acrylic acids, anhydrides, and derivatives thereof, such as their  $\rm C_1\text{-}C_5$  alkyl esters, lower alkyl-substituted acrylic acids, e.g.,  $\rm C_1\text{-}C_2$  substituted acrylic acids, such as methacrylic acid, 2-ethylacrylic acid, etc., and their  $\rm C_1\text{-}C_4$  alkyl esters, unless clearly indicated otherwise. The terms "(meth)acrylic" or "(meth)acrylate" are intended to cover both the acrylic/acrylate and methacrylic/methacrylate forms of the indicated material, e.g., a (meth)acrylate monomer. The term "(meth)acrylic polymer" refers to polymers prepared from one or more (meth)acrylic monomers.

As used herein molecular weights are determined by gel permeation chromatography using a polystyrene standard. Unless otherwise indicated molecular weights are on a weight average basis.

The term "glass transition temperature" is a theoretical value being the glass transition temperature as calculated by the method of Fox on the basis of monomer composition of the monomer charge according to T. G. Fox, Bull. Am. Phys. Soc. (Ser. II) 1, 123 (1956) and J. Brandrup, E. H. Immergut, Polymer Handbook 3<sup>rd</sup> edition, John Wiley, New York, 1989.

As used herein, unless otherwise defined, the term substantially free means that the component is present, if at all, in an amount of less than 5% by weight, based on the total weight of the slurry composition.

As used herein, unless otherwise defined, the term essentially free means that the component is present, if at all, in an amount of less than 1% by weight, based on the total weight of the slurry composition.

As used herein, unless otherwise defined, the term completely free means that the component is not present in the slurry composition, i.e., 0.00% by weight, based on the total weight of the slurry composition.

As used herein, the term "total solids" refers to the non-volatile components of the slurry composition of the present invention and specifically excludes the organic medium

As used herein, the term "consists essentially of" includes 5 the recited material or steps and those that do not materially affect the basic and novel characteristics of the claimed invention

As used herein, the term "consists of" excludes any element, step or ingredient not recited.

For purposes of the detailed description, it is to be understood that the invention may assume various alternative variations and step sequences, except where expressly specified to the contrary. Moreover, other than in any operating examples, or where otherwise indicated, all numbers such as those expressing values, amounts, percentages, ranges, subranges and fractions may be read as if prefaced by the word "about," even if the term does not expressly appear. Accordingly, unless indicated to the contrary, the 20 numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the 25 scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Where a closed or open-ended numerical range is described herein, all numbers, values, amounts, percentages, 30 subranges and fractions within or encompassed by the numerical range are to be considered as being specifically included in and belonging to the original disclosure of this application as if these numbers, values, amounts, percentages, subranges and fractions had been explicitly written out 35 in their entirety.

Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard variation found in their respective testing measurements.

As used herein, unless indicated otherwise, a plural term can encompass its singular counterpart and vice versa, 45 unless indicated otherwise. For example, although reference is made herein to "an" electrochemically active material, "a" fluoropolymer, "a" dispersant, and "a" conductive carbon material, a combination (i.e., a plurality) of these components can be used. In addition, in this application, the use of 50 "or" means "and/or" unless specifically stated otherwise, even though "and/or" may be explicitly used in certain instances

As used herein, "including," "containing" and like terms are understood in the context of this application to be 55 synonymous with "comprising" and are therefore openended and do not exclude the presence of additional undescribed or unrecited elements, materials, ingredients or method steps. As used herein, "consisting of" is understood in the context of this application to exclude the presence of 60 any unspecified element, ingredient or method step. As used herein, "consisting essentially of" is understood in the context of this application to include the specified elements, materials, ingredients or method steps "and those that do not materially affect the basic and novel characteristic(s)" of 65 what is being described. Although various embodiments of the invention have been described in terms of "comprising",

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embodiments consisting essentially of or consisting of are also within the scope of the present invention.

As used herein, the terms "on," "onto," "applied on," "applied onto," "formed on," "deposited on," "deposited onto," mean formed, overlaid, deposited, or provided on but not necessarily in contact with the surface. For example, a composition "deposited onto" a substrate does not preclude the presence of one or more other intervening coating layers of the same or different composition located between the electrodepositable coating composition and the substrate.

Whereas specific embodiments of the invention have been described in detail, it will be appreciated by those skilled in the art that various modifications and alternatives to those details could be developed in light of the overall teachings of the disclosure. Accordingly, the particular arrangements disclosed are meant to be illustrative only and not limiting as to the scope of the invention which is to be given the full breadth of the claims appended and any and all equivalents thereof.

#### Aspects

Each of the characteristics and examples described above, and combinations thereof, may be said to be encompassed by the present invention. The present invention is thus drawn in particular, without being limited thereto, to the following aspects:

- 1. A slurry composition comprising:
- (a) a binder comprising a polymer comprising a fluoropolymer dispersed in a liquid medium; and
- (b) at least one conductive carbon material having a BET surface area of greater than 100 m<sup>2</sup>/g.
- 2. The slurry composition of Aspect 1, wherein the conductive carbon material has a BET surface area of  $100.1~\text{m}^2/\text{g}$  to  $1,000~\text{m}^2/\text{g}$  such as  $150~\text{m}^2/\text{g}$  to  $600~\text{m}^2/\text{g}$  or  $100.1~\text{m}^2/\text{g}$  to  $400~\text{m}^2/\text{g}$  or  $200~\text{m}^2/\text{g}$  to  $400~\text{m}^2/\text{g}$ .
- The slurry composition of Aspect 1, wherein the conductive carbon material has a BET surface area of about 200 m<sup>2</sup>/g.
- 4. The slurry composition of any one of Aspects 1 to 3, wherein the conductive carbon material is carbon black.
- 5. The slurry composition of any one of Aspects 1 to 4, wherein the slurry has a total solids content of 55 percent by weight or greater and a viscosity of no more than 4000 cP as measured by an Anton-Paar rheometer having a model number MCR301 using a 50-millimeter cone and temperature-controlled plate at 25° C.
- The slurry composition of any one of Aspects 1 to 5, further comprising (c) an electrochemically active material
- 7. The slurry composition of Aspect 6, wherein
- (a) the binder is present in amounts of 2 to 20 percent by weight;
- (b) the conductive carbon material is present in amounts of 2 to 20 percent by weight; and
- (c) the electrochemically active material is present in amounts of 45 to 96 percent by weight; the percentages by weight being based on total solids weight.
- 8. The slurry composition of Aspects 6 or 7, wherein the electrochemically active material comprises a material capable of incorporating lithium.
- The slurry composition of Aspect 8, wherein the material capable of incorporating lithium comprises LiCoO<sub>2</sub>, LiNiO<sub>2</sub>, LiFePO<sub>4</sub>, LiCoPO<sub>4</sub>, LiMnO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, Li(NiMnCo)O<sub>2</sub>, Li(NiCoAl)O<sub>2</sub>, carboncoated LiFePO<sub>4</sub>, or a combination thereof.

- 10. The slurry composition of Aspects 6 or 7, wherein the electrochemically active material comprises a material capable of lithium conversion.
- 11. The slurry composition of Aspect 10, wherein the material capable of lithium conversion comprises sulfur, LiO<sub>2</sub>, FeF<sub>2</sub> and FeF<sub>3</sub>, Si, aluminum, tin, SnCo, Fe<sub>3</sub>O<sub>4</sub>, or combinations thereof.
- 12. The slurry composition of Aspects 6 or 7, wherein the electrochemically active material comprises graphite, silicon compounds, tin, tin compounds, sulfur, sulfur 10 compounds, or a combination thereof.
- 13. The slurry composition of any one of Aspects 1 to 12, wherein the fluoropolymer comprises a (co)polymer comprising the residue of vinylidene fluoride.
- 14. The slurry composition of Aspect 13, wherein the 15 fluoropolymer comprises a polyvinylidene fluoride homopolymer.
- 15. The slurry composition of any one of Aspects 1 to 14, further comprising a dispersant.
- 16. The slurry composition of Aspect 15, wherein the 20 dispersant comprises a (meth)acrylic polymer.
- 17. The slurry composition of Aspect 16, wherein the (meth)acrylic polymer further comprises constitutional units comprising the residue of an epoxy functional ethylenically unsaturated monomer, vinyl pyrrolidone, 25 or combinations thereof.
- 18. The slurry composition of Aspect 17, wherein the (meth)acrylic polymer comprises at least one epoxy functional group, and the epoxy functional group is post-reacted with a beta-hydroxy functional acid.
- 19. The slurry composition of any one of Aspects 16 to 18, wherein the liquid medium comprises an organic medium, and the (meth)acrylic polymer prepared by conventional free radical initiated solution polymerization of a mixture of ethylenically unsaturated monomers dissolved in a second organic medium.
- 20. The slurry composition of Aspect 19, wherein the second organic medium used to prepare the (meth) acrylic polymer is the same as the organic medium of the slurry composition.
- The slurry composition of Aspects 19 or 20, wherein the second organic medium comprises a trialkylphosphate.
- 22. The slurry composition of any one of Aspects 15 to 21, wherein polyvinylidene fluoride polymer and the dispersant are not bound by a covalent bond.
- 23. The slurry composition of any one of Aspects 15 to 22, wherein the composition further comprises a crosslinker.
- 24. The slurry composition of any one of Aspects 16 to 22, 50 wherein the (meth)acrylic polymer is self-crosslinking.
- 25. The slurry composition of any one of Aspects 1 to 24, wherein the liquid medium comprises an organic medium.
- 26. The slurry composition of Aspect 25, wherein the 55 organic medium has an evaporation rate less than 10 g/min m<sup>2</sup>, at the dissolution temperature of the fluoropolymer in the organic medium.
- 27. The slurry composition of Aspects 25 or 26, wherein the organic medium has an evaporation rate greater  $^{60}$  than  $^{80}$  g/min  $^{2}$ , at  $^{180}$ ° C.
- 28. The slurry composition of any one of Aspects 25 to 27, wherein the organic medium comprises butyl pyrrolidone, trialkyl phosphate such as triethyl phosphate, 1,2,3-triacetoxypropane, 3-methoxy-N,N-dimethylpropanamide, ethyl acetoacetate, gamma-butyrolactone, propylene glycol methyl ether, or combinations thereof.

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- 29. The slurry composition of Aspect 28, wherein the organic medium comprises trialkyl phosphate such as triethyl phosphate and an additional solvent.
- 30. The slurry composition of any one of Aspects 1 to 29, further comprising an adhesion promoter.
- 31. The slurry composition of any one of Aspects 1 to 30, wherein the slurry composition has a solids content of 10% to 90% by weight, 20% to 60% by weight, such as 30% to 70% by weight, such as 40% to 65% by weight, such as 50% to 60% by weight, such as 30% to 90% by weight, such as 40% to 85% by weight, such as 50% to 85% by weight, such as 60% to 85% by weight, such as 65% to 85% by weight, such as 65% to 85% by weight, such as 71% to 85% by weight, such as 75% to 85% by weight, based on the total weight of the slurry composition.
- 32. The slurry composition of any one of Aspects 6 to 30, wherein the slurry composition has a viscosity below 5,000 cp as measured by an Anton-Paar rheometer having a model number MCR301 using a 50 millimeter cone and temperature-controlled plate at 25° C. and a solids content of 55% to 85% by weight, such as 60% to 85% by weight, such as 65% to 85% by weight, such as 71% to 85% by weight, such as 75% to 85% by weight, such as 65% to 75% by weight, such as 68% to 72% by weight, based on the total weight of the slurry composition.
- 33. The slurry composition of any one of Aspects 1 to 32, wherein the slurry is substantially free of isophorone.
- 34. The slurry composition of any one of Aspects 1 to 33, wherein the slurry is substantially free of N-methyl-2pyrrolidone.
- 35. An electrode comprising:
- (a) an electrical current collector; and
- (b) a film formed on the electrical current collector, wherein the film is deposited from the slurry composition of any one of Aspects 6 to 34.
- 36. The electrode of Aspect 35, wherein the electrical current collector (a) comprises copper or aluminum in the form of a mesh, sheet or foil.
- 37. The electrode of Aspects 35 or 36, wherein the electrode comprises a positive electrode.
- 38. The electrode of Aspects 35 or 36, wherein the electrode comprises a negative electrode.
- 39. The electrode of any one of Aspects 35 to 38, wherein the film is cross-linked.
- 40. The electrode of any one of Aspects 35 to 39, wherein the electrical current collector is pretreated with a pretreatment composition.
- 41. The electrode of any one of Aspect 35 to 40, wherein the film has a thickness of at least 1  $\mu$ m, such as 1 to 500  $\mu$ m, such as 1 to 150  $\mu$ m, such as 25 to 150  $\mu$ m, such as 30 to 125  $\mu$ m.
- 42. The electrode of any one of Aspect 35 to 41, wherein the film has a uniform composition.
- 43. An electrical storage device comprising:
- (a) the electrode of any one of Aspect 35 to 42;
- (b) a counter electrode; and
- (c) an electrolyte.
- 44. The electrical storage device of Aspect 43, wherein the electrolyte (c) comprises a lithium salt dissolved in a solvent.
- 45. The electrical storage device of Aspect 44, wherein the lithium salt is dissolved in an organic carbonate.
- 46. The electrical storage device of any one of Aspects 43 to 45, wherein the electrical storage device comprises a cell.

- 47. The electrical storage device of any one of Aspects 43 to 45, wherein the electrical storage device comprises a battery pack.
- 48. The electrical storage device of any one of Aspects 43 to 45, wherein the electrical storage device comprises <sup>5</sup> a secondary battery.
- 49. The electrical storage device of any one of Aspects 43 to 45, wherein the electrical storage device comprises a capacitor.
- 50. The electrical storage device of any one of Aspects 43 to 45, wherein the electrical storage device comprises a supercapacitor.

Illustrating the invention are the following examples that are not to be construed as limiting the invention to their details. All parts and percentages in the Examples as well as throughout the specification are by weight unless otherwise indicated.

#### **EXAMPLES**

The viscosities in the Examples were measured with an Anton-Paar MCR301 rheometer using a 50-millimeter cone and temperature-controlled plate at a temperature of 25° C.

#### Example 1

Synthesis of (meth)acrylic polymer dispersant with theoretical glass transition (Tg) of 58° C. Table 1 lists the synthesis charge components with amounts added:

TABLE 1

	Ingredients	Amount (gram)
Charge 1:	Methylether of propylene glycol	658
Charge 2:	methyl methacrylate	1121.1
(premixed)	ethyl acrylate	435.9
	hydroxyl ethyl acrylate	33.2
	methacrylic acid	33.15
Charge 3:	Tertiary amyl peroxy 2-ethyl hexyl carbonate	33.8
(premixed)	methylether of propylene glycol	169.6
Charge 4:	Tertiary amyl peroxy 2-ethyl hexyl carbonate	11.9
(premixed)	methylether of propylene glycol	169.6
Charge 5:	methylether of propylene glycol	584.6

To a suitable reaction vessel equipped with a stirrer, reflux 45 condenser, thermometer, heating mantle and nitrogen inlet. Charge 1 was added at ambient temperatures. The temperature was then increased to reflux (~120° C.), at which time the monomer premix of Charge 3 was added over 185 minutes. 5 minutes after the start of charge 3, charge 2 was 50 added over 180 minutes. Upon completion of charge 2 and 3, charge 4 was added over 60 minutes, followed by a hold for additional 60 minutes at reflux (~120° C.). Thereafter the reaction temperature was cooled to 40° C. and Charge 5 was added with a subsequent 30 minute hold period. The (meth) 55 acrylic polymer dispersant composition thus formed had a theoretical solid content of 52% by weight.

Solids contents of dispersant compositions were measured in each dispersant example by the following procedure. An aluminum weighing dish from Fisher Scientific, 60 was weighed using an analytical balance. The weight of the empty dish was recorded to four decimal places. Approximately 0.5 g of dispersant and 3.5 g of acetone was added to the weigh dish. The weight of the dish and the dispersant solution was recorded to four decimal places. The dish 65 containing the dispersant solution was placed into a laboratory oven, with the oven temperature set to 110 degrees

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centigrade, and dried for 1 hour. The weigh dish and dried dispersant was weighed using an analytical balance. The weight of the dish and dried dispersant was recorded to four decimal places. The solids was determined using the following equation: % solids=100×[(weight of the dish and the dry dispersant)-(weight of the empty dish)]/[(weight of the dish and the dispersant solution)-(weight of the empty dish)].

#### Example 2

Synthesis of acrylic polymer with theoretical glass transition (Tg) of -12° C.: This polymer was prepared the same way as the polymer of Example 1 except 30% of methyl methacrylate was replaced by 2-ethyl hexyl acrylate.

#### Example 3

Preparation of a Binder Dispersion

In a plastic container was placed 224.4 grams of trieth-ylphosphate and 31.6 grams of (meth)acrylic copolymer dispersant composition from Example 2. The resulting mixture was stirred vigorously using a Cowles blade while maintaining a modest vortex. This mixing was continued while 144 grams of polyvinylidene difluoride powder, PVDF T-1 (Inner Mongolia Wanhao Fluorochemical Co., Ltd.) was added in small portions. Mixing was continued for an additional 20 minutes after all the polyvinylidene difluoride powder was added. The binder dispersion had a volume weighted mean particle size of 218 nm by dynamic light scattering method.

#### Example 4

Preparation of a Binder Dispersion with Crosslinking Agent
 To a plastic container was added 0.41 grams of a melamine crosslinking agent (Cymel 303 available from CYTEC, lot KZKGMP002) and 50.0 grams of the binder dispersion from Example 3. This mixture was agitated with

 a dual asymmetric mixer at 2000 RPM for 5 minutes.

#### Example 5

Preparation of a Binder Dispersion with Crosslinking Agent In a plastic container was placed 224.4 grams of triethylphosphate and 31.6 grams of (meth)acrylic copolymer dispersant composition from Example 1. The resulting mixture was stirred vigorously using a Cowles blade while maintaining a modest vortex. This mixing was continued while 144 grams of polyvinylidene difluoride powder, PVDF T-1 (Inner Mongolia Wanhao Fluorochemical Co., Ltd.) was added in small portions. Mixing was continued for an additional 20 minutes after all the polyvinylidene difluoride powder was added. This dispersion had a volume weighted mean particle size of 326 nm by dynamic light scattering method. To this dispersion was added slowly 3.27 grams of a melamine crosslinking agent (Cymel 303 available from CYTEC, lot KZKGMP002) while mixing with a Cowels blade for 10 minutes.

#### Example 6

Preparation of a Binder Dispersion

In a plastic container was placed 299.2 grams of triacetin and 123.2 grams of the (meth)acrylic copolymer dispersant composition from Example 1. The resulting mixture was stirred vigorously using a Cowles blade while maintaining a

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modest vortex. This mixing was continued while 177.6 grams of polyvinylidene difluoride powder, PVDF T-1 (Inner Mongolia Wanhao Fluorochemical Co., Ltd.) was added in small portions. Mixing was continued for an additional 20 minutes after all the polyvinylidene difluoride powder was added. This dispersion had a volume weighted mean particle size of 351 nm by dynamic light scattering method.

#### Example 7

Preparation of a Binder with Crosslinking Agent

To a plastic container was added 1.05 grams of melamine crosslinking agent (Cymel 303 available from CYTEC, lot KZKGMP002) and 50.0 grams of the binder dispersion from Example 6. This mixture was agitated with a dual asymmetric mixer at 2000 RPM for 5 minutes.

#### Example 8

Preparation of a Comparative Binder

To a plastic container was added 1000 grams of N-methyl pyrrolidone. While mixing with a cowels blade, 64 grams of polyvinylidene difluoride powder, PVDF T-1 (Inner Mongolia Wanhao Fluorochemical Co., Ltd) was added in small portions. Mixing was continued until all powder was dissolved. The solution was allowed to stand to allow entrained air to dissipate.

#### Example 9

Preparation of Comparative Binder

To a plastic container was added 760 grams of N-methyl pyrrolidone. While mixing with a cowels blade, 40 grams of polyvinylidene difluoride powder, PVDF T-1 (Inner Mongolia Wanhao Fluorochemical Co., Ltd.) was added in small 35 portions. Mixing was continued until all powder was dissolved. The solution was allowed to stand to allow entrained air to dissipate.

#### Example 10

Preparation of a Comparative Slurry

To a plastic cup was added triethylphosphate (14.1 grams) and the binder dispersion from Example 4 (1.50 grams). Conductive carbon Timcal C-NERGYTM Super C65 (0.45 45 grams) having a BET surface area of 62 m<sup>2</sup>/g as measured according to ASTM D3037-89 was added in two portions with each sequential blend mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes. Cathode active powder NMC-111 (14.0 grams, electrochemically active 50 material (Li(NiMnCo)O<sub>2</sub>), available from BASF) was added in two portions with each resulting combination sequentially mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes to produce formulated slurry. The total nonvolatiles content of this slurry was 50.0% by weight, and 55 viscosity of this slurry was 1280 cP under a shear rate of 10 reciprocal seconds and 528 cP under a shear rate of 100 reciprocal seconds.

Solids contents for all compositions other than the dispersant compositions were measured by the following procedure. An aluminum weighing dish from Fisher Scientific, was weighed using an analytical balance. The weight of the empty dish was recorded to four decimal places. Approximately 1 g of dispersion was added to the weigh dish. The weight of the dish and the wet dispersion was recorded to 65 four decimal places. The dish containing the slurry was placed into a laboratory oven, with the oven temperature set

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to 120 degrees centigrade, and dried for 1 hour. The weigh dish and dried dispersion was weighed using an analytical balance. The weight of the dish and dried slurry was recorded to four decimal places. The solids was determined using the following equation: % solids=100×[(weight of the dish and the dry dispersion)–(weight of the empty dish)]/ [(weight of the dish and the wet dispersion)–(weight of the empty dish)].

#### Example 11

Preparation of a Comparative Slurry

To a plastic cup was added triethylphosphate (12.5 grams) and the binder dispersion from Example 4 (1.65 grams). Conductive carbon Super C65 (0.49 grams) was added in two portions with each sequential blend mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes. Cathode active powder NMC-111 (15.3 grams) was added in two portions with each resulting combination sequentially mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes to produce formulated slurry. The total non-volatiles content of this slurry was 55.0% by weight, and viscosity of this slurry was 1804 cP under a shear rate of 10 reciprocal seconds and 807 cP under a shear rate of 100 reciprocal seconds.

#### Example 12

Preparation of a Comparative Slurry

To a plastic cup was added triethylphosphate (10.9 grams) and the binder dispersion from Example 4 (1.80 grams). Conductive carbon Super C65 (0.54 grams) was added in two portions with each sequential blend mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes.
 Cathode active powder NMC-111 (16.7 grams) was added in two portions with each resulting combination sequentially mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes to produce formulated slurry. The total non-volatiles content of this slurry was 60.0% by weight, and viscosity of this slurry was 6691 cP under a shear rate of 10 reciprocal seconds and 2000 cP under a shear rate of 100 reciprocal seconds.

#### Example 13

Preparation of Slurry

To a plastic cup was added triethylphosphate (14.1 grams) and the binder dispersion from Example 4 (1.50 grams). Conductive carbon LITX 200 (0.45 grams) was added in two portions with each sequential blend mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes. Cathode active powder NCM-111 (14.0 grams) was added in two portions with each resulting combination sequentially mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes to produce formulated slurry. The total non-volatiles content of this slurry was 50.0% by weight, and viscosity of this slurry was 513 cP under a shear rate of 10 reciprocal seconds and 298 cP under a shear rate of 100 reciprocal seconds.

#### Example 14

Preparation of Slurry

To a plastic cup was added triethylphosphate (12.5 grams) and the binder dispersion from Example 4 (1.65 grams). Conductive carbon LITX 200 (0.49 grams) was added in two portions with each sequential blend mixed in a dual-asym-

metric centrifugal mixer at 2000 rpm for 5 minutes. Cathode active powder NMC-111 (15.3 grams) was added in two portions with each resulting combination sequentially mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes to produce formulated slurry. The total non-volatiles content of this slurry was 55.0% by weight, and viscosity of this slurry was 1146 cP under a shear rate of 10 reciprocal seconds and 639 cP under a shear rate of 100 reciprocal seconds.

#### Example 15

Preparation of Slurry

To a plastic cup was added triethylphosphate (10.9 grams) and the binder dispersion from Example 4 (1.80 grams).

Conductive carbon LITX 200 (0.54 grams) was added in two portions with each sequential blend mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes. Cathode active powder NMC-111 (16.7 grams) was added in two portions with each resulting combination sequentially mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes to produce formulated slurry. The total non-volatiles content of this slurry was 60.0% by weight, and viscosity of this slurry was 1473 cP under a shear rate of 10 reciprocal seconds and 913 cP under a shear rate of 100 reciprocal seconds.

#### Example 16

Preparation of Slurry

To a plastic cup was added triethylphosphate (9.3 grams) and the binder dispersion from Example 4 (1.95 grams). Conductive carbon LITX 200 (0.59 grams) was added in two portions with each sequential blend mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes. Cathode active powder NMC-111 (18.1 grams) was added in two portions with each resulting combination sequentially mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes to produce formulated slurry. The total non-volatiles content of this slurry was 65.0% by weight, and viscosity of this slurry was 2799 cP under a shear rate of 10 reciprocal seconds and 1791 cP under a shear rate of 100 reciprocal seconds.

#### Example 17

Preparation of a Comparative Slurry

To a plastic cup was added NMP (6.5 grams) and the binder composition from Example 9 (24.69 grams). Conductive carbon Super C65 (0.90 grams) was added in one 50 portion and the blend mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 10 minutes. Cathode active powder NMC-111 (27.9 grams) was added in one portion and the resulting combination mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 10 minutes to produce 55 formulated slurry. The total non-volatiles content of this slurry was 50.0% by weight, and viscosity of this slurry was 1588 cP under a shear rate of 10 reciprocal seconds and 545 cP under a shear rate of 100 reciprocal seconds.

#### Example 18

Preparation of a Comparative Slurry

To a plastic cup was added NMP (2.2 grams) and the binder composition from Example 9 (17.45 grams). Conductive carbon Super C65 (0.64 grams) was added in one portion and the blend mixed in a dual-asymmetric centrifu-

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gal mixer at 2000 rpm for 10 minutes. Cathode active powder NMC-111 (19.7 grams) was added in one portion and the resulting combination mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 10 minutes to produce formulated slurry. The total non-volatiles content of this slurry was 53.0% by weight, and viscosity of this slurry was 3620 cP under a shear rate of 10 reciprocal seconds and 1057 cP under a shear rate of 100 reciprocal seconds.

#### Example 19

Preparation of a Comparative Slurry

To a plastic cup was added the binder composition from Example 9 (18.46 grams). Conductive carbon Super C65 (0.67 grams) was added in one portion and the blend mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 10 minutes. Cathode active powder NMC-111 (20.9 grams) was added in one portion and the resulting combination mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 10 minutes to produce formulated slurry. The total non-volatiles content of this slurry was 56.1% by weight, and viscosity of this slurry was 4462 cP under a shear rate of 10 reciprocal seconds and 1390 cP under a shear rate of 100 reciprocal seconds.

#### Example 20

Preparation of Comparative Slurry

To a plastic cup was added NMP (5.6 grams) and the binder composition from Example 8 (9.97 grams). Conductive carbon LITX 200 (0.45 grams) was added in two portions with each sequential blend mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes. Cathode active powder NMC-111 (14.0 grams) was added in two portions with each resulting combination sequentially mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes to produce formulated slurry. The total non-volatiles content of this slurry was 50.1% by weight, and viscosity of this slurry was 1988 cP under a shear rate of 10 reciprocal seconds and 611 cP under a shear rate of 100 reciprocal seconds.

#### Example 21

45 Preparation of Comparative Slurry

To a plastic cup was added NMP (3.2 grams) and the binder composition from Example 8 (6.26 grams). Conductive carbon LITX 200 (0.49 grams) was added in two portions with each sequential blend mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes. Cathode active powder NMC-111 (15.3 grams) was added in two portions with each resulting combination sequentially mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes to produce formulated slurry. The total non-volatiles content of this slurry was 55.1% by weight, and viscosity of this slurry was 3390 cP under a shear rate of 10 reciprocal seconds and 1218 cP under a shear rate of 100 reciprocal seconds.

#### Example 22

Preparation of Comparative Slurry

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To a plastic cup was added NMP (0.0 grams) and the binder composition from Example 8 (6.26 grams). Conductive carbon LITX 200 (0.54 grams) was added in two portions with each sequential blend mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes. Cathode

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active powder NMC-111 (16.7 grams) was added in two portions with each resulting combination sequentially mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes to produce formulated slurry. The total non-volatiles content of this slurry was 60.1% by weight, and viscosity of 5 this slurry was 6557 cP under a shear rate of 10 reciprocal seconds and 2209 cP under a shear rate of 100 reciprocal seconds.

#### Example 23

Preparation of a Comparative Slurry

To a plastic cup was added Triacetin (14.3 grams) and the binder dispersion from Example 7 (1.26 grams). Conductive carbon Super C65 (0.45 grams) was added in two portions with each sequential blend mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes. Cathode active powder NMC-111 (1395.0 grams) was added in two portions with each resulting combination sequentially mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes to produce formulated slurry. The total non-volatiles content of this slurry was 50.0% by weight, and viscosity of this slurry was 1066 cP under a shear rate of 10 reciprocal seconds and 246 cP under a shear rate of 100 reciprocal seconds.

#### Example 24

Preparation of a Comparative Slurry

To a plastic cup was added Triacetin (12.8 grams) and the binder dispersion from Example 7 (1.39 grams). Conductive carbon Super C65 (0.49 grams) was added in two portions with each sequential blend mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes. Cathode active powder NMC-111 (15.4 grams) was added in two portions with each resulting combination sequentially mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes to produce formulated slurry. The total non-volatiles content of this slurry was 55.0% by weight, and viscosity of this slurry was 2145 cP under a shear rate of 10 reciprocal seconds and 463 cP under a shear rate of 100 reciprocal seconds.

### Example 25

Preparation of a Comparative Slurry

To a plastic cup was added Triacetin (11.2 grams) and the binder dispersion from Example 7 (1.51 grams). Conductive carbon Super C65 (0.54 grams) was added in two portions with each sequential blend mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes. Cathode active powder NMC-111 (16.7 grams) was added in two portions with each resulting combination sequentially mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes to produce formulated slurry. The total non-volatiles content of this slurry was 60.0% by weight, and viscosity of this slurry was 5495 cP under a shear rate of 10 reciprocal seconds and 990 cP under a shear rate of 100 reciprocal seconds.

#### Example 26

Preparation of Slurry

To a plastic cup was added Triacetin (14.3 grams) and the binder dispersion from Example 7 (1.26 grams). Conductive 65 carbon LITX 200 (0.45 grams) was added in two portions with each sequential blend mixed in a dual-asymmetric

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centrifugal mixer at 2000 rpm for 5 minutes. Cathode active powder NMC-111 (14.0 grams) was added in two portions with each resulting combination sequentially mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes to produce formulated slurry. The total non-volatiles content of this slurry was 50.0% by weight, and viscosity of this slurry was 260 cP under a shear rate of 10 reciprocal seconds and 88 cP under a shear rate of 100 reciprocal seconds.

#### Example 27

Preparation of Slurry

To a plastic cup was added Triacetin (12.8 grams) and the binder dispersion from Example 7 (1.39 grams). Conductive carbon LITX 200 (0.50 grams) was added in two portions with each sequential blend mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes. Cathode active powder NMC-111 (15.4 grams) was added in two portions with each resulting combination sequentially mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes to produce formulated slurry. The total non-volatiles content of this slurry was 55.0% by weight, and viscosity of this slurry was 449 cP under a shear rate of 10 reciprocal seconds and 123 cP under a shear rate of 100 reciprocal seconds.

#### Example 28

Open Preparation of Slurry

To a plastic cup was added Triacetin (11.2 grams) and the binder dispersion from Example 7 (1.51 grams). Conductive carbon LITX 200 (0.54 grams) was added in two portions with each sequential blend mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes. Cathode active powder NMC-111 (16.7 grams) was added in two portions with each resulting combination sequentially mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes to produce formulated slurry. The total non-volatiles content of this slurry was 60.0% by weight, and viscosity of this slurry was 929 cP under a shear rate of 10 reciprocal seconds and 206 cP under a shear rate of 100 reciprocal seconds.

#### Example 29

Preparation of Slurry

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To a plastic cup was added Triacetin (9.6 grams) and the binder dispersion from Example 7 (1.64 grams). Conductive carbon LITX 200 (0.59 grams) was added in two portions with each sequential blend mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes. Cathode active powder NMC-111 (18.1 grams) was added in two portions with each resulting combination sequentially mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes to produce formulated slurry. The total non-volatiles content of this slurry was 65.0% by weight, and viscosity of this slurry was 1975 cP under a shear rate of 10 reciprocal seconds and 368 cP under a shear rate of 100 reciprocal seconds.

#### Example 30

Preparation of Slurry

To a plastic cup was added Triacetin (8.1 grams) and the binder dispersion from Example 7 (1.77 grams). Conductive carbon LITX 200 (0.63 grams) was added in two portions

with each sequential blend mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes. Cathode active powder NMC-111 (19.5 grams) was added in two portions with each resulting combination sequentially mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes to produce formulated slurry. The total non-volatiles content of this slurry was 70.0% by weight, and viscosity of this slurry was 4942 cP under a shear rate of 10 reciprocal seconds and 760 cP under a shear rate of 100 reciprocal seconds

#### Example 31

Preparation of Comparative Slurry and Electrode

To a plastic cup was added NMP (3.4 grams) and the binder composition from Example 8 (22.62 grams). Conductive carbon LITX 200 (1.06 grams) was added in two portions with each sequential blend mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes. Cathode active powder NMC-111 (32.9 grams) was added in two portions with each resulting combination sequentially mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes to produce formulated slurry. The total non-volatiles content of this slurry was 59.0% by weight.

A wet film was prepared on pre-cleaned aluminum foil by a draw-down application of this formulated slurry using a doctor blade. This wet film was heated in an oven to a maximum temperature of 110° C. for at least 4 minutes. After cooling, an average dry film thickness of 46 microns was determined from five measurements with a micrometer. Battery performance data for this coating is shown in Table 2

#### Example 32

Preparation of Slurry and Electrode

To a plastic cup was added triacetin (13.5 grams) and the binder dispersion from Example 7 (2.95 grams). Conductive carbon LITX 200 (1.05 grams) was added in two portions 40 with each sequential blend mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes. Cathode active powder NMC-111 (32.6 grams) was added in two portions with each resulting combination sequentially mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes to produce formulated slurry. The total non-volatiles content of this slurry was 70.0% by weight.

A wet film was prepared on pre-cleaned aluminum foil by a draw-down application of this formulated slurry using a doctor blade. This wet film was heated in an oven to a 50 maximum temperature of 180° C. for at least 4 minutes. After cooling, an average dry film thickness of 45 microns was determined from five measurements with a micrometer. Battery performance data for this coating is shown in Table

#### Example 33

Preparation of Slurry and Electrode

To a plastic cup was added triethylphosphate (16.7 grams) 60 and the binder dispersion from Example 5 (4.09 grams). Conductive carbon LITX 200 (1.22 grams) was added in two portions with each sequential blend mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5 minutes. Cathode active powder NMC-111 (37.9 grams) was added in two 65 portions with each resulting combination sequentially mixed in a dual-asymmetric centrifugal mixer at 2000 rpm for 5

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minutes to produce formulated slurry. The total non-volatiles content of this slurry was 68.0% by weight.

A wet film was prepared on pre-cleaned aluminum foil by a draw-down application of this formulated slurry using a doctor blade. This wet film was heated in an oven to a maximum temperature of 110° C. for at least 4 minutes. After cooling, an average dry film thickness of 49 microns was determined from five measurements with a micrometer.

TABLE 2

		Initial cycle			
Example	0.2 C	1.0 C	1.6 C	6.4 C	loss (%)
Example 31 (comparative)	136	113	101	48	19
Example 32 Example 33	139 139	125 120	117 109	63 38	14 15

Coin cell evaluation comparing high solids coatings prepared with high surface area conductive carbon. Results show similar or better performance for higher solids formulations of present invention.

It will be appreciated by skilled artisans that numerous modifications and variations are possible in light of the above disclosure without departing from the broad inventive concepts described and exemplified herein. Accordingly, it is therefore to be understood that the foregoing disclosure is merely illustrative of various exemplary aspects of this application and that numerous modifications and variations can be readily made by skilled artisans which are within the spirit and scope of this application and the accompanying claims

What is claimed is:

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- 1. A slurry composition comprising:
- (a) a binder comprising a polymer comprising a fluoropolymer dispersed in an organic medium comprising a primary solvent and a co-solvent; and
- (b) at least one conductive carbon material having a BET surface area of greater than 100 m<sup>2</sup>/g,
- wherein the organic medium is substantially free of water.
- The slurry composition of claim 1, wherein the conductive carbon material has a BET surface area of 100.1
   m²/g to 1,000 m²/g.
  - 3. The slurry composition of claim 1, wherein the conductive carbon material has a BET surface area of 200 m<sup>2</sup>/g.
  - **4**. The slurry composition of claim **1**, further comprising an electrochemically active material.
    - 5. The slurry composition of claim 4, wherein
    - (a) the binder is present in amounts of 2 to 20 percent by weight;
    - (b) the conductive carbon material is present in amounts of 2 to 20 percent by weight; and
    - (c) the electrochemically active material is present in amounts of 45 to 96 percent by weight; the percentages by weight being based on total solids weight.
  - **6**. The slurry composition of claim **4**, wherein the electrochemically active material comprises a material capable of incorporating lithium comprising LiCoO<sub>2</sub>, LiNiO<sub>2</sub>, LiFePO<sub>4</sub>, LiCoPO<sub>4</sub>, LiMnO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, Li(NiMnCo)O<sub>2</sub>, Li(NiCoAl)O<sub>2</sub>, carbon-coated LiFePO<sub>4</sub>, or a combination thereof.
  - 7. The slurry composition of claim 4, wherein the electrochemically active material comprises a material capable of lithium conversion comprising sulfur, LiO<sub>2</sub>, FeF<sub>2</sub>, FeF<sub>3</sub>, Si, aluminum, tin, SnCo, Fe<sub>3</sub>O<sub>4</sub>, or combinations thereof.

- 8. The slurry composition of claim 4, wherein the electrochemically active material comprises graphite, silicon compounds, tin, tin compounds, sulfur, sulfur compounds, or a combination thereof.
- **9**. The slurry composition of claim **1**, wherein the fluoropolymer comprises a polyvinylidene fluoride polymer.
- 10. The slurry composition of claim 1, further comprising a dispersant comprising an addition polymer.
- 11. The slurry composition of claim 10, wherein the addition polymer comprises a (meth)acrylic polymer comprising constitutional units comprising a residue of methyl methacrylate and constitutional units comprising a residue of ethylenically unsaturated monomer comprising a heterocyclic group.
- 12. The slurry composition of claim 10, wherein the composition further comprises a cross-linker.
- $1\overline{3}$ . The slurry composition of claim 1, wherein the organic medium has an evaporation rate less than 10 g/min  $m^2$ , at the dissolution temperature of the fluoropolymer dispersed in the organic medium.
- 14. The slurry composition of claim 1, wherein the primary solvent comprises butyl pyrrolidone, a trialkylphosphate, 3-methoxy-N,N-dimethylpropanamide, 1,2,3-triac-

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etoxypropane, or a combination thereof, and the co-solvent comprises ethyl acetoacetate, gamma-butyrolactone, and/or glycol ethers.

- 15. The slurry composition of claim 1, wherein the primary solvent comprises triethyl phosphate and the cosolvent comprises ethyl acetoacetate.
- 16. The slurry composition of claim 1, further comprising an adhesion promoter.
  - 17. An electrode comprising:
  - (a) an electrical current collector; and
  - (b) a film formed on the electrical current collector, wherein the film is deposited from the slurry composition of claim 4.
- 18. The electrode of claim 17, wherein the film is cross- 15 linked.
  - 19. An electrical storage device comprising:
  - (a) the electrode of claim 18;
  - (b) a counter electrode; and
  - (c) an electrolyte.
  - 20. The electrical storage device of claim 19, wherein the electrical storage device comprises a cell, a battery pack, a secondary battery, a capacitor, or a supercapacitor.

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