



(51) International Patent Classification:

H01M 4/62 (2006.01) *C08L 27/16* (2006.01)
H01M 4/04 (2006.01) *C08L 27/18* (2006.01)
H01M 4/131 (2010.01) *C08L 27/20* (2006.01)
H01M 4/1391 (2010.01) *H01M 4/02* (2006.01)

(21) International Application Number:

PCT/US2023/019220

(22) International Filing Date:

20 April 2023 (20.04.2023)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

63/332,806 20 April 2022 (20.04.2022) US

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(54) Title: FLUOROPOLYMER BINDER FOR LITHIUM-ION SECONDARY BATTERY CATHODE

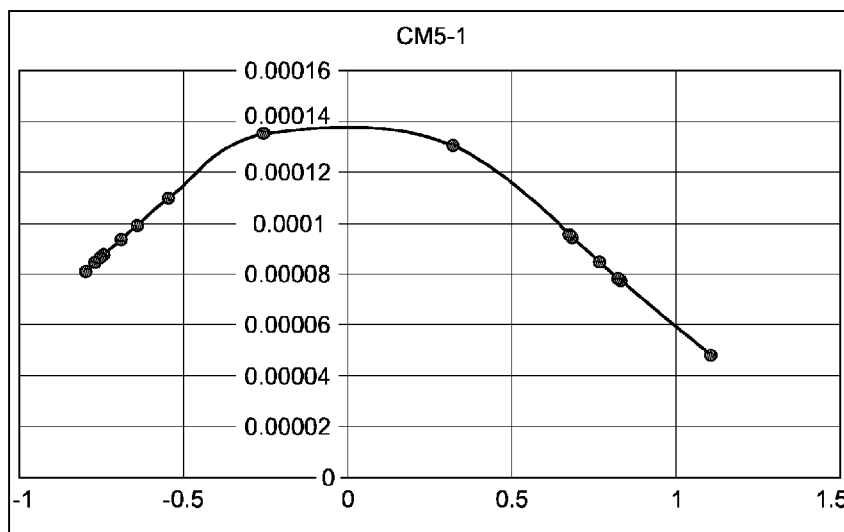


Figure 1

(57) **Abstract:** A fluoropolymer binder composition is provided for use in a lithium-ion secondary battery cathode, containing tetrafluoroethylene polymer and elastomeric fluoropolymer. Cathode compositions are also provided containing this fluoropolymer binder composition together with cathode active particles and conductive carbon. The tetrafluoroethylene polymer is generally a high molecular weight non-melt fabricable tetrafluoroethylene homopolymer and modified tetrafluoroethylene homopolymer. The elastomeric fluoropolymer is generally a vinylidene fluoride elastomeric fluoropolymer. The cathode composition is formed by a process free from solvent, by dry mixing the fluoropolymer binder, cathode active and conductive carbon, and applying a shear force, whereby the tetrafluoroethylene polymer is fibrillated. The cathode compositions have fluoropolymer binder homogeneously dispersed in the major component cathode active, and have elasticity such that thin films of the cathode compositions can be formed into a cylindrical shape without fracture, enabling their utility as lithium-ion battery cathode electrode films.



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(81) **Designated States** (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) **Designated States** (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

TITLE

FLUOROPOLYMER BINDER FOR LITHIUM-ION SECONDARY BATTERY CATHODE

FIELD

[0001] The present invention relates to a fluoropolymer binder composition for use in a lithium-ion secondary battery cathode and a method of producing the same.

SUMMARY

[0002] The present invention provides a fluoropolymer binder composition for use in a lithium-ion secondary battery cathode, comprising: i.) tetrafluoroethylene polymer and ii.) elastomeric fluoropolymer (alternately referred to herein as fluoroelastomer). The tetrafluoroethylene polymer is generally selected from high molecular weight non-melt fabricable tetrafluoroethylene homopolymer, and high molecular weight non-melt fabricable modified tetrafluoroethylene homopolymer. The elastomeric fluoropolymer is generally a vinylidene fluoride elastomeric fluoropolymer. The binder composition is formed by a process free from solvent, generally, by dry mixing the tetrafluoroethylene polymer and the elastomeric fluoropolymer, and in one embodiment, applying a shear force to the composition, whereby the tetrafluoroethylene polymer is fibrillated.

[0003] The present invention further provides a cathode composition for use in a lithium-ion secondary battery cathode, comprising: the aforementioned fluoropolymer binder composition, further containing cathode active particles and conductive carbon. The present cathode composition has elasticity such that a calendared film of the composition suitable for use as a cathode electrode film in a lithium-ion battery can be formed into a tubular shape without fracture.

[0004] The present invention further provides a method for manufacturing the aforementioned cathode composition for use in a lithium-ion secondary battery cathode, comprising mixing elastomeric fluoropolymer, cathode active particles, tetrafluoroethylene polymer and conductive carbon to form the cathode composition. In one embodiment the method involves mixing elastomeric fluoropolymer and cathode active particles to form a fluoroelastomer and cathode active composition, then mixing

this composition with tetrafluoroethylene polymer and conductive carbon to form the cathode composition. The steps of the present method of mixing are carried out free from solvent, and generally involve dry mixing and applying a shear force to the composition of fluoroelastomer, cathode active particles, tetrafluoroethylene polymer and conductive carbon, whereby the shear force is sufficient such that said tetrafluoroethylene polymer is fibrillated.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] Figure 1, Figure 2, Figure 3 and Figure 4 are fluorine content distribution plots obtained from LIBS microscopy carried out on films of present compositions of cathode active, tetrafluoroethylene polymer and elastomeric fluoropolymer.

DETAILED DESCRIPTION

[0006] In one embodiment the present invention is a fluoropolymer binder composition for use in a lithium-ion secondary battery cathode, comprising: i.) tetrafluoroethylene polymer, and ii.) elastomeric fluoropolymer.

[0007] In another embodiment the present invention is a cathode composition for use in a lithium-ion secondary battery cathode, comprising: i.) tetrafluoroethylene polymer, ii.) elastomeric fluoropolymer, iii.) cathode active particles, and iv.) conductive carbon.

[0008] In one embodiment the cathode composition has elasticity such that a calendared film of the composition suitable for use as a cathode electrode film in a lithium-ion battery can be formed into a tubular shape without fracture.

[0009] In one embodiment the present tetrafluoroethylene polymer has a melt creep viscosity of at least about 1.8×10^{11} poise. In another embodiment, tetrafluoroethylene polymer has a melt creep viscosity of at least about 2.0×10^{11} poise. In another embodiment, tetrafluoroethylene polymer has a melt creep viscosity of at least about 3.0×10^{11} poise. In a preferred embodiment, tetrafluoroethylene polymer has a melt creep viscosity of at least about 4.0×10^{11} poise. Herein, melt creep viscosity (MCV) is measured by the method described in Ebnesajjad, Sina, (2015), Fluoroplastics, Volume 1 - Non-Melt Processible Fluoropolymers - The Definitive User's Guide and Data Book

(2nd Edition), Appendix 5, Melt Creep Viscosity of Polytetrafluoroethylene, pp. 660-661, with reference to US patent 3,819,594.

[0010] The present tetrafluoroethylene polymer is a polymer comprising repeating units of tetrafluoroethylene monomer, also referred to in this field as TFE, and has a melt creep viscosity of at least about 1.8×10^{11} poise. With such high melt viscosity, the polymer does not flow in the molten state and therefore is not a melt-processible polymer. In one embodiment, the tetrafluoroethylene polymer is a tetrafluoroethylene homopolymer, containing only repeating units of the tetrafluoroethylene monomer, also known in this field as polytetrafluoroethylene, abbreviated as PTFE. In another embodiment the tetrafluoroethylene polymer is a "modified" PTFE, referring to copolymers of TFE with such small concentrations of comonomer that the melting point of the resultant polymer is not substantially reduced below that of PTFE. The concentration of such comonomer is less than 1 wt %, preferably less than 0.5 wt %. A minimum amount of at least about 0.05 wt % is used to have significant effect. Example comonomer of modified PTFE include perfluoroolefins, notably hexafluoropropylene (HFP) or perfluoro(alkyl vinyl ether) (PAVE), where the alkyl group contains 1 to 5 carbon atoms, with perfluoro(ethyl vinyl ether) (PEVE) and perfluoro(propyl vinyl ether) (PPVE) being preferred. Further examples of comonomers of modified PTFE include chlorotrifluoroethylene (CTFE) and perfluorobutyl ethylene (PFBE), or other similar monomers that introduce bulky side groups into the polymer chain.

[0011] In a preferred embodiment the present tetrafluoroethylene polymer is fibrillatable. By fibrillatable is meant that the tetrafluoroethylene polymer is capable of forming nanosized in at least one dimension (i.e. <100 nm width) fibrils which can vary in length from submicron to several microns in length when the tetrafluoroethylene polymer is exposed to shear, e.g., during the present mixing method for manufacturing a cathode composition.

[0012] In one embodiment the present elastomeric fluoropolymer has a Mooney viscosity of at least about 20 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646. In another embodiment the present elastomeric fluoropolymer has a Mooney viscosity of at least about 30 MU measured under

conditions ML 1 + 10 (121°C) according to ASTM D1646. In another embodiment the present elastomeric fluoropolymer has a Mooney viscosity of at least about 40 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646. In another embodiment the present elastomeric fluoropolymer has a Mooney viscosity of at least about 50 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646. In another embodiment the present elastomeric fluoropolymer has a Mooney viscosity of at least about 60 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646. In a preferred embodiment the elastomeric fluoropolymer has a Mooney viscosity of at least about 70 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.

[0013] The present elastomeric fluoropolymer are elastomers, that provide elasticity to the present cathode composition such that a calendared film of the composition can be formed into a tubular shape without fracture, e.g., a tubular shape having a radius of curvature sufficient for utility as cathode electrode film in a lithium-ion battery.

[0014] Example elastic fluoropolymers include: vinylidene fluoride/hexafluoropropylene (VDF/HFP), vinylidene fluoride/hexafluoropropylene/tetrafluoroethylene (VDF/HFP/TFE), vinylidene fluoride/perfluoro(methyl vinyl ether)/tetrafluoroethylene (VDF/PMVE/TFE), tetrafluoroethylene/perfluoro(methyl vinyl ether) (TFE/PMVE), tetrafluoroethylene/propylene (TFE/P) and ethylene/tetrafluoroethylene/perfluoro(methyl vinyl ether) (E/TFE/PMVE).

[0015] Alternately, elastic fluoropolymers of utility in the present invention can be described as:

(A) VDF-based elastic fluoropolymers, in which VDF is copolymerized with at least one additional comonomer selected from the group consisting of:

(i) C2-C8 perfluoroolefins, such as tetrafluoroethylene (TFE), hexafluoropropylene (HFP);

- (ii) hydrogen-containing C2-C8 olefins, such as vinyl fluoride (VF), trifluoroethylene, hexafluoroisobutene, perfluoroalkyl ethylenes of formula $\text{CH}_2=\text{CH-R}_f$, wherein R_f is a C1-C6 perfluoroalkyl group;
 - (iii) C2-C8 fluoroolefins comprising at least one of iodine, chlorine and bromine, such as chlorotrifluoroethylene (CTFE);
 - (iv) (per)fluoroalkylvinylethers (PAVE) of formula $\text{CF}_2=\text{CFOR}_f$, wherein R_f is a C1-C6 (per)fluoroalkyl group, preferably $-\text{CF}_3$, $-\text{C}_2\text{F}_5$, $-\text{C}_3\text{F}_7$;
 - (v) (per)fluoro-oxy-alkylvinylethers of formula $\text{CF}_2=\text{CFOX}$, wherein X is a C1-C12 ((per)fluoro)-oxyalkyl comprising catenary oxygen atoms, e.g. the perfluoro-2-propoxypropyl group;
 - (vi) (per)fluorodioxoles;
 - (vii) (per)fluoro-methoxy-vinylethers having formula: $\text{CF}_2=\text{CFOCF}_2\text{OR}_f$, wherein R_f is selected from the group consisting of C1-C6 (per)fluoroalkyls; C5-C6 cyclic (per)fluoroalkyls; and C2-C6 (per)fluoroalkyls, comprising at least one catenary oxygen atom; R_f is preferably $-\text{CF}_2\text{CF}_3$; $-\text{CF}_2\text{CF}_2\text{OCF}_3$; or $-\text{CF}_3$;
 - (viii) C2-C8 non-fluorinated olefins, for example ethylene and propylene; and
- (2) TFE-based elastic fluoropolymers, in which TFE is copolymerized with at least one additional comonomer selected from the group consisting of (i) through (vii) as described immediately above.

[0016] In a preferred embodiment the elastic fluoropolymer is a vinylidene fluoride copolymer, more preferably a vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene copolymer.

[0017] In one embodiment the elastomeric fluoropolymer binder is crosslinked. Crosslinking not only improves the mechanical properties of the polymer, but also helps provide good contact between the components of the present cathode composition.

[0018] In a preferred embodiment, the fluoropolymer binder composition comprises tetrafluoroethylene homopolymer having a melt creep viscosity of at least about 4.0 x

10¹¹ poise, and the elastomeric fluoropolymer is a vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene copolymer having Mooney viscosity of at least about 17 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.

[0019] In one embodiment, the weight ratio of the tetrafluoroethylene polymer to the elastomeric fluoropolymer in the present binder and cathode composition is from about 4:1 to about 1:4. In a preferred embodiment, the weight ratio of the tetrafluoroethylene polymer to said elastomeric fluoropolymer is about 1:1. The amount of elastomeric fluoropolymer in the cathode composition can be determined within this range by one of average skill in this field, and is preferably the minimal amount necessary for a film of the present cathode composition to satisfactorily perform in a cathode having a radius of curvature necessary for a given lithium-ion battery.

[0020] In one embodiment of the present cathode composition, the amount of the fluoropolymer binder is from about 2 to about 10 weight percent, the amount of the cathode active particles is from about 90 to about 97 weight percent, and the amount of the conductive carbon is from about 0.1 to about 5 weight percent, based on the combined weight of the fluoropolymer binder, the cathode active particles, and the conductive carbon.

[0021] In one embodiment, the amount of the tetrafluoroethylene polymer in the cathode composition is about 2 weight percent, the amount of the elastomeric fluoropolymer is about 2 weight percent, the amount of the cathode active particles is about 95 weight percent, and the amount of the conductive carbon is about 1 weight percent, based on the combined weight of the fluoropolymer binder, the cathode active particles, and the conductive carbon. In one embodiment, the amount of the tetrafluoroethylene polymer in the cathode composition is about 1 weight percent, the amount of the elastomeric fluoropolymer is about 1 weight percent, the amount of the cathode active particles is about 97 weight percent, and the amount of the conductive carbon is about 1 weight percent, based on the combined weight of the fluoropolymer binder, the cathode active particles, and the conductive carbon.

[0022] The present cathode active particles are selected from electrochemical cathode active materials known in this field. Example cathode active particles include metal oxide, metal sulfide, or a lithium metal oxide. In a preferred embodiment, the cathode active particles comprise a lithium transition metal oxide. Example lithium metal oxides include: lithium nickel manganese cobalt oxide (NMC), lithium manganese oxide (LMO), lithium iron phosphate (LiFePO_4), lithium cobalt oxide (LCO), lithium titanate (LTO), and/or lithium nickel cobalt aluminum oxide (NCA). In some embodiments, cathode active materials can comprise, for example, a layered transition metal oxide (such as LiCoO_2 (LCO), $\text{Li}(\text{NiMnCo})\text{O}_2$ (NMC), $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA)), spinel manganese oxide (such as LiMn_2O_4 (LMO), $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LMNO)) or an olivine (such as LiFePO_4), LiNiO_2 , $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$, $\text{LiNi}_{0.85}\text{Co}_{0.1}\text{Al}_{0.05}\text{O}_2$, $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$, LiMn_2O_4 , and combinations thereof.

[0023] The present conductive carbon is selected from electro-conductive carbon materials known in this field. Example conductive carbon materials of utility in the present invention include carbon black, porous carbon, carbon nanotubes, carbon fiber, VGCF (vapor grown carbon fiber), graphene sheets, acetylene black, and combinations thereof.

[0024] In one embodiment the present invention is a method for manufacturing a cathode composition for use in a lithium-ion secondary battery cathode, comprising, mixing elastomeric fluoropolymer, cathode active particles, tetrafluoroethylene polymer and conductive carbon to form the cathode composition.

[0025] In one embodiment, prior to mixing with any other component of the cathode composition, the elastomeric fluoropolymer is masticated at elevated temperature (e.g., from about 80°C to about 150°C) sufficient to impart fluidity to the elastomeric fluoropolymer. The present inventors discovered that the elastic fluoropolymer in a less viscous and semi-fluid state, then subsequently mixing with the cathode active particles, conductive carbon and tetrafluoroethylene polymer, results in a cathode composition having all components substantially homogeneously dispersed. Without wishing to be bound by theory, the present inventors believe that the elastomeric fluoropolymer in a semi-fluid or fluid state when forming the present cathode composition acts as a viscous

lubricant which is compatible with the tetrafluoroethylene polymer, improving the mixing of the cathode composition components (shown in the present experimental results by shorter mixer torque peak times) and improving dispersion of the cathode composition components (shown in the present experimental results by improved Laser Induced Breakdown Spectroscopy (LIBS) results.)

[0026] In one embodiment the present invention is a method for manufacturing a cathode composition for use in a lithium-ion secondary battery cathode, comprising: i.) mixing an elastomeric fluoropolymer and cathode active particles to form a fluoroelastomer and cathode active composition, and ii.) mixing the fluoroelastomer and cathode active composition with a tetrafluoroethylene polymer, to form the cathode composition. In one embodiment of this method, the starting form of the elastomeric fluoropolymer is pellets or sheet. In one embodiment, prior to the step i.) mixing of the elastomeric fluoropolymer and cathode active, the elastomeric fluoropolymer pellets or sheet are masticated at elevated temperature (e.g., from about 80°C to about 150°C) sufficient to impart fluidity to the elastomeric fluoropolymer, resulting in the pellets or sheet combining into one homogeneous continuous semi-fluid mass of elastomeric fluoropolymer, which results in better mixing and substantially homogenous dispersion of the elastomeric fluoropolymer throughout the cathode active.

[0027] In an alternate embodiment, in mixing step i.), fluoroelastomer and cathode active composition is a concentrate containing from about 1 to about 5 weight percent fluoroelastomer, and from about 90 to about 97 weight percent cathode active particles, and then additional elastomeric fluoropolymer is added in mixing step ii.).

[0028] In a preferred embodiment, the mixing steps are carried out free from solvent. Alternately stated, the mixing steps are carried out by dry mixing, wherein the components of the cathode composition are in a dry form, e.g., agglomerates, granules, beads, pellets, sheet or powder.

[0029] In one embodiment, mixing step ii.) is carried out by applying a shear force to the composition of fluoroelastomer, cathode active particles, tetrafluoroethylene polymer and conductive carbon, whereby the shear force is sufficient such that said tetrafluoroethylene polymer is fibrillated.

[0030] In one embodiment, the temperature of the mixing steps is from about 80°C to about 150°C. In another embodiment, the temperature of the mixing steps is about 120°C.

[0031] In one embodiment the mixing steps are carried out in a mixer, wherein the fill factor is from about 75% to about 95%, and the maximum mixing torque occurs within about 0.5 to about 3 minutes of initiating mixing. Mixers of utility in the present method can be easily determined by the person of average skill in this field and include mixers capable of generating high shear forces and generally applicable for homogeneously mixing plastic and rubber materials.

[0032] In the present method, the degree of dispersion of the tetrafluoroethylene polymer and fluoroelastomer in the cathode composition resulting from the mixing steps can be determined by Laser Induced Breakdown Spectroscopy (LIBS). The degree of dispersion of the tetrafluoroethylene polymer and fluoroelastomer in the cathode composition is desirably sufficiently high, so as to enable the cathode composition to be suitable for use as a cathode electrode film in a lithium-ion battery.

[0033] In a one preferred embodiment, the degree of dispersion of the tetrafluoroethylene polymer and fluoroelastomer in the cathode composition results in a cathode composition having sufficient elasticity such that a calendared film of the cathode composition can be formed into a tubular shape without failure, for example, fracture, cracking, crazing, or other structural discontinuities that could result in poor cathode performance.

EXAMPLES

[0034] MATERIALS

- a. Cathode active: LMO (lithium manganese oxide) dry powder, supplier Posco Es Materials
- b. PTFE1 (P1): tetrafluoroethylene homopolymer dry powder, melt creep viscosity of 4.0×10^{11} poise, supplier Chemours FC LLC

- c. PTFE2 (P2): modified tetrafluoroethylene dry powder, melt creep viscosity of 1.8×10^{11} poise, supplier Chemours FC LLC
- d. PTFE3 (P3): modified tetrafluoroethylene dry powder, melt creep viscosity of 1.3×10^{10} poise, supplier Chemours FC LLC
- e. Fluoroelastomer1 (F1): VDF/HFP copolymer pellets or sheet, Mooney viscosity 65 MU measured under conditions ML 1 + 10 (100°C) according to ASTM D1646, supplier Chemours FC LLC
- f. Fluoroelastomer2 (F2): VDF/HFP/TFE copolymer pellets or sheet, Mooney viscosity 75 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646, supplier Chemours FC LLC
- g. Fluoroelastomer3 (F3): VDF/TFE/PMVE copolymer pellets or sheet, Mooney viscosity 65 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646, supplier Chemours FC LLC
- h. Fluoroelastomer4 (F4): VDF/HFP/TFE copolymer pellets or sheet, Mooney viscosity 23 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646, supplier Chemours FC LLC

PROCEDURE

[0035] Amounts of elastomeric fluoropolymer (rubbery/elastic pellets or sheet) were added to a Brabender mixer for mastication at 120°C at 60 RPM for a period of 1 minute to generate a less viscous and semi-fluid continuous mass of elastomeric fluoropolymer. Amounts of cathode active particles were then added to the Brabender mixer to mix with the semi-fluid elastomeric fluoropolymer and distribute the elastomeric fluoropolymer homogeneously throughout the cathode active particle matrix. The mixing was carried out at 120°C at 60 RPM for a period of 0.5 minute. Amounts of tetrafluoroethylene polymer binder powder were then added to the Brabender mixer to mix with the previously-formed cathode active particle and elastomeric fluoropolymer mixture, to distribute the tetrafluoroethylene polymer binder powder homogeneously throughout the cathode active particle matrix, and to fibrillate the tetrafluoroethylene polymer. The

mixing was carried out at 120°C at 60 RPM for a period of time sufficient to observe the MPT (peak torque maximum time (minutes)) and MPTQ (maximum peak torque (kgf.m)), evidence of fibrillation of the tetrafluoroethylene polymer, and then mixing was continued under these conditions for an additional 5 minutes. The formed cathode mixture was then removed from the mixer, cooled to room temperature and observed visually (by the naked eye) and by SEM (scanning electron microscope) to assess degree of mixing, dispersion of the elastomeric fluoropolymer and tetrafluoroethylene polymer throughout the cathode active particle continuous phase, and to assess extent of fibrillation of the tetrafluoroethylene polymer. A portion of the so-formed cathode mixture was taken and pressed at a temperature of from 120°C to 200°C to form a 200 micrometer thick film. The resultant film was then observed visually (by the naked eye), by SEM (scanning electron microscope) and by Laser Induced Breakdown Spectroscopy (LIBS) microscope.

[0036] For the purposes of enabling analysis of dispersion of the cathode composition components by SEM and LIBS, conductive carbon was excluded from these example compositions, as it complicated and obscured the sample analysis by SEM and/or LIBS. However, when included in the cathode compositions, the conductive carbon did not substantially otherwise change the observed experimental mixing, dispersion and fibrillation results.

RESULTS

[0037] Table 1 Key: Ex = Example number; C = cathode active (wt%); P1 = PTFE1 (wt%); P2 = PTFE2 (wt%); P3 = PTFE3 (wt%); F1 = Fluoroelastomer1 (wt%); F2 = Fluoroelastomer2 (wt%); F3 = Fluoroelastomer3 (wt%); F4 = Fluoroelastomer4 (wt%); FF = mixer fill factor (% of mixer volume); MPT = peak torque maximum time (minutes); MPTQ = maximum peak torque (kgf.m); ST = set temperature of mixer (°C); CT = mixer chamber measured temperature (°C)

Table 1

Ex	C	P1	P2	P3	F1	F2	F3	F4	FF	MPT	MPTQ	ST	CT	Comment
1	97	3							85	3	23.5	150	143.0	LIBS data CM-7 (Figure 3)
2	95		5						90	20	20.0	150	150.5	NA
3	95	2.5			2.5				85	0.5	15.0	120	143.2	NA
4	97	2			1				85	1	13.2	120	142.3	NA
5	97		2		1				85	4	9.1	120	138.8	NA
6	97			2	1				85	15	0.0	120	138.1	no torque increase
7	97	2				1			85	1	15.3	120	145.2	NA
8	97	2					1		85	1.5	15.2	120	142.0	NA
9	97	2				1			75	2	12.3	150	138.1	NA
10	97	2				1			85	1	13.4	150	145.1	NA
11	97	2				1			95	0.5	15.6	150	139.2	LIBS data CM 5-1 (Figure1)
12	97	2				1			85	1	15.4	120	112.9	LIBS data CM5-2 (Figure 2)
13	97	2						1	85	1.5	12.4	120	116.1	LIBS data CM 9 (Figure 4)
14	97					3			85	25	0.0	150	138.4	no torque increase

[0038] In all examples shown in Table 1, the RPM (revolutions per minute) setting of the mixer was 60 RPM.

[0039] Example 11 is a composition of: 97 wt% cathode active (LMO), 2 wt% PTFE1 (P1) (tetrafluoroethylene homopolymer dry powder, relatively high melt creep viscosity of 4.0×10^{11} poise), and 1 wt% Fluoroelastomer2 ((F2) (VDF/HFP/TFE copolymer, relatively high Mooney viscosity 75 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646). The mixer fill factor is 95%, the mixer peak torque maximum time is 0.5 minutes, the mixer maximum peak torque is 15.6 kgf.m, the mixer set temperature is 150°C, and the mixer chamber measured temperature is 139.2°C. Figure 1 is the fluorine content distribution plot obtained from LIBS microscopy carried out on a film of Example 11 composition. This plot shows that the fluoropolymer binder components of this composition are effectively homogeneously dispersed through the

major component cathode active. A 200 micrometer thick film of Example 11 composition is found to have sufficient elasticity such that it can be formed into a tubular shape without fracture and so has utility as a cathode electrode film in a lithium-ion battery.

[0040] Example 12 is identical to Example 11, except that the mixer fill factor is 85%, the mixer peak torque maximum time is 1 minutes, the mixer maximum peak torque is 15.4 kgf.m, the mixer set temperature is 120°C, and the mixer chamber measured temperature is 112.9°C. Figure 2 is the fluorine content distribution plot obtained from LIBS microscopy carried out on a film of Example 12 composition. This plot shows that the fluoropolymer binder components of this composition are very effectively homogeneously dispersed through the major component cathode active. A 200 micrometer thick film of Example 12 composition is found to have sufficient elasticity such that it can be formed into a tubular shape without fracture and so has utility as a cathode electrode film in a lithium-ion battery.

[0041] Example 1 is a comparative composition of: 97 wt% cathode active (LMO) and 3 wt% PTFE1 (P1) (tetrafluoroethylene homopolymer dry powder, relatively high melt creep viscosity of 4.0×10^{11} poise) containing no elastomeric fluoropolymer. The mixer fill factor is 85%, the mixer peak torque maximum time is 3 minutes, the mixer maximum peak torque is 23.5 kgf.m, the mixer set temperature is 150°C, and the mixer chamber measured temperature is 143.0°C. Figure 3 is the fluorine content distribution plot obtained from LIBS microscopy carried out on a film of Example 1 composition. This plot shows that the fluoropolymer binder components of this composition, in the absence of elastomeric fluoropolymer, are not effectively dispersed through the major component cathode active in the present dry mixing process. A 200 micrometer thick film of Example 1 composition is found to have insufficient elasticity such that it cannot be formed into a tubular shape without fracture and so is unlikely to have utility as a cathode electrode film in a lithium-ion battery.

[0042] Example 13 is a comparative composition of: 97 wt% cathode active (LMO) and 2 wt% PTFE1 (P1) (tetrafluoroethylene homopolymer dry powder, relatively high melt creep viscosity of 4.0×10^{11} poise) and 1 wt% Fluoroelastomer4 ((F4):

VDF/HFP/TFE copolymer pellets or sheet, Mooney viscosity 23 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.) The mixer fill factor is 85%, the mixer peak torque maximum time is 1.5 minutes, the mixer maximum peak torque is 12.4 kgf.m, the mixer set temperature is 120°C, and the mixer chamber measured temperature is 116.1°C. Figure 4 is the fluorine content distribution plot obtained from LIBS microscopy carried out on a film of Example 13 composition. This plot shows that the fluoropolymer binder components of this composition are not effectively dispersed through the major component cathode active in the present dry mixing process by using an elastomeric fluoropolymer having relatively low Mooney viscosity. A 200 micrometer thick film of Example 13 composition is found to have insufficient elasticity such that it cannot be formed into a tubular shape without fracture and so is unlikely to have utility as a cathode electrode film in a lithium-ion battery.

CLAIMS

What is claimed is:

1. A fluoropolymer binder composition for use in a lithium-ion secondary battery cathode, comprising: i.) tetrafluoroethylene polymer, and; ii.) elastomeric fluoropolymer.
2. The binder composition of claim 1, wherein said tetrafluoroethylene polymer has a melt creep viscosity of at least about 1.8×10^{11} poise.
3. The binder composition of claim 1, wherein said tetrafluoroethylene polymer has a melt creep viscosity of at least about 2.0×10^{11} poise.
4. The binder composition of claim 1, wherein said tetrafluoroethylene polymer has a melt creep viscosity of at least about 3.0×10^{11} poise.
5. The binder composition of claim 1, wherein said tetrafluoroethylene polymer has a melt creep viscosity of at least about 4.0×10^{11} poise.
6. The binder composition of claim 1, wherein said elastomeric fluoropolymer has a Mooney viscosity of at least about 20 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.
7. The binder composition of claim 1, wherein said elastomeric fluoropolymer has a Mooney viscosity of at least about 30 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.
8. The binder composition of claim 1, wherein said elastomeric fluoropolymer has a Mooney viscosity of at least about 40 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.
9. The binder composition of claim 1, wherein said elastomeric fluoropolymer has a Mooney viscosity of at least about 50 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.

10. The binder composition of claim 1, wherein said elastomeric fluoropolymer has a Mooney viscosity of at least about 60 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.
11. The binder composition of claim 1, wherein said elastomeric fluoropolymer has a Mooney viscosity of at least about 70 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.
12. The binder composition of claim 1, wherein said elastomeric fluoropolymer is a vinylidene fluoride elastomeric fluoropolymer.
13. The binder composition of claim 1, wherein said vinylidene fluoride elastomeric fluoropolymer comprises a vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene copolymer.
14. The binder composition of claim 1, wherein said tetrafluoroethylene polymer is a tetrafluoroethylene homopolymer.
15. The binder composition of claim 1, wherein said tetrafluoroethylene polymer is selected from the group consisting of high molecular weight non-melt fabricable tetrafluoroethylene homopolymer and high molecular weight non-melt fabricable modified tetrafluoroethylene homopolymer.
16. The binder composition of claim 1, wherein said tetrafluoroethylene polymer is a tetrafluoroethylene homopolymer having a melt creep viscosity of at least about 4.0×10^{11} poise, and said elastomeric fluoropolymer is a vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene copolymer having Mooney viscosity of at least about 17 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.
17. The binder composition of claim 1, wherein the weight ratio of said tetrafluoroethylene polymer to said elastomeric fluoropolymer is from about 4:1 to about 1:4.
18. The binder composition of claim 1, wherein said tetrafluoroethylene polymer is fibrillated.

19. The binder composition of claim 1, formed by a process free from solvent.
20. The binder composition of claim 1, wherein said composition is formed by dry mixing said tetrafluoroethylene polymer and said elastomeric fluoropolymer.
21. The binder composition of claim 1, wherein said composition is formed by dry mixing said tetrafluoroethylene polymer and said elastomeric fluoropolymer, and applying a shear force to said composition, whereby said tetrafluoroethylene polymer is fibrillated.
22. A cathode composition for use in a lithium-ion secondary battery cathode, comprising: i.) fluoropolymer binder comprising a mixture of tetrafluoroethylene polymer and elastomeric fluoropolymer; ii.) cathode active particles; and iii.) conductive carbon; said cathode composition having an elasticity such that a calendared film of said composition suitable for use as a cathode electrode film in a lithium-ion battery can be formed into a tubular shape without fracture.
23. The cathode composition of claim 22, wherein said cathode active particles comprise lithium transition metal oxide.
24. The binder composition of claim 1, wherein said tetrafluoroethylene polymer has a melt creep viscosity of at least about 1.8×10^{11} poise.
25. The cathode composition of claim 22, wherein said tetrafluoroethylene polymer has a melt creep viscosity of at least about 2.0×10^{11} poise.
26. The cathode composition of claim 22, wherein said tetrafluoroethylene polymer has a melt creep viscosity of at least about 3.0×10^{11} poise.
27. The cathode composition of claim 22, wherein said tetrafluoroethylene polymer has a melt creep viscosity of at least about 4.0×10^{11} poise.
28. The cathode composition of claim 22, wherein said elastomeric fluoropolymer has a Mooney viscosity of at least about 20 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.

29. The cathode composition of claim 22, wherein said elastomeric fluoropolymer has a Mooney viscosity of at least about 30 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.
30. The cathode composition of claim 22, wherein said elastomeric fluoropolymer has a Mooney viscosity of at least about 40 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.
31. The cathode composition of claim 22, wherein said elastomeric fluoropolymer has a Mooney viscosity of at least about 50 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.
32. The cathode composition of claim 22, wherein said elastomeric fluoropolymer has a Mooney viscosity of at least about 60 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.
33. The cathode composition of claim 22, wherein said elastomeric fluoropolymer has a Mooney viscosity of at least about 70 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.
34. The cathode composition of claim 22, wherein said elastomeric fluoropolymer is a vinylidene fluoride elastomeric fluoropolymer.
35. The cathode composition of claim 22, wherein said vinylidene fluoride elastomeric fluoropolymer comprises a vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene copolymer.
36. The cathode composition of claim 22, wherein said tetrafluoroethylene polymer is a tetrafluoroethylene homopolymer.
37. The cathode composition of claim 22, wherein said tetrafluoroethylene polymer is selected from the group consisting of high molecular weight non-melt fabricable tetrafluoroethylene homopolymer and high molecular weight non-melt fabricable modified tetrafluoroethylene homopolymer.

38. The cathode composition of claim 22, wherein said tetrafluoroethylene polymer is a tetrafluoroethylene homopolymer having a melt creep viscosity of at least about 4.0×10^{11} poise, and said elastomeric fluoropolymer is a vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene copolymer having Mooney viscosity of at least about 17 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.
39. The cathode composition of claim 22, wherein the amount of said fluoropolymer binder in said cathode composition is from about 5 to about 10 weight percent, the amount of said cathode active particles is from about 90 to about 97 weight percent, and the amount of said conductive carbon is from about 0.1 to about 1 weight percent, based on the combined weight of said fluoropolymer binder, said cathode active particles, and said conductive carbon.
40. The cathode composition of claim 22, wherein the amount of said tetrafluoroethylene polymer is about 2 weight percent, the amount of said elastomeric fluoropolymer is about 1 weight percent, the amount of said cathode active particles is about 96 weight percent, and the amount of said conductive carbon is about 1 weight percent, based on the combined weight of said fluoropolymer binder, said cathode active particles, and said conductive carbon.
41. The cathode composition of claim 22, wherein said tetrafluoroethylene polymer is fibrillated.
42. The cathode composition of claim 22, formed by a process free from solvent.
43. The cathode composition of claim 22, wherein said composition is formed by dry mixing said tetrafluoroethylene polymer, said elastomeric fluoropolymer, said cathode active particles and said conductive carbon.
44. The cathode composition of claim 22, wherein said composition is formed by dry mixing said tetrafluoroethylene polymer, said elastomeric fluoropolymer, said cathode active particles and said conductive carbon, and applying a shear force to said composition, whereby said tetrafluoroethylene polymer is fibrillated.

45. A method for manufacturing a cathode composition for use in a lithium-ion secondary battery cathode, comprising mixing elastomeric fluoropolymer, cathode active particles, tetrafluoroethylene polymer and conductive carbon to form said cathode composition.
46. The method of claim 45, wherein prior to said mixing, said elastomeric fluoropolymer is masticated at elevated temperature sufficient to impart fluidity to said elastomeric fluoropolymer.
47. The method of claim 46, wherein said elevated temperature is from about 80°C to about 150°C.
48. The method of claim 45, comprising: i.) mixing said elastomeric fluoropolymer and said cathode active particles to form a fluoroelastomer and cathode active composition; and ii.) mixing said fluoroelastomer and cathode active composition with a tetrafluoroethylene polymer and conductive carbon; to form said cathode composition.
49. The method of claim 48, wherein prior to said step i.) mixing, said elastomeric fluoropolymer is masticated at elevated temperature sufficient to impart fluidity to said elastomeric fluoropolymer.
50. The method of claim 49, wherein said elevated temperature is from about 80°C to about 150°C.
51. The method of claim 48, wherein the step i.) fluoroelastomer and cathode active composition is a concentrate containing from about 1 to about 5 weight percent fluoroelastomer, and from about 90 to about 97 weight percent cathode active, and wherein additional elastomeric fluoropolymer is added in step ii.).
52. The method of claim 45, wherein said cathode composition contains from about 1 to about 5 weight percent tetrafluoroethylene polymer, from about 1 to about 5 weight percent elastomeric fluoropolymer, from about 90 to about 97 weight percent cathode active, and from about 0.1 to about 1 weight percent conductive carbon.

53. The method of claim 45, wherein the weight ratio of said tetrafluoroethylene polymer to said elastomeric fluoropolymer is from about 4:1 to about 1:4.
54. The method of claim 45, wherein said mixing is carried out free from solvent.
55. The method of claim 45, wherein said mixing is carried out by dry mixing.
56. The method of claim 45, wherein said mixing is carried out by applying a shear force to the composition of fluoroelastomer, cathode active particles, tetrafluoroethylene polymer and conductive carbon, whereby said shear force is sufficient such that said tetrafluoroethylene polymer is fibrillated.
57. The method of claim 45, wherein said mixing is carried out at a temperature of from about 80°C to about 150°C.
58. The method of claim 45, wherein said mixing is carried out at a temperature of about 120°C.
59. The method of claim 45, wherein said mixing is carried out in a mixer, the fill factor is from about 75% to about 95%, and the maximum mixing torque occurs within about 0.5 to about 3 minutes of initiating mixing.
60. The method of claim 45, wherein the degree of dispersion of said tetrafluoroethylene polymer and said fluoroelastomer in said cathode composition as determined by Laser Induced Breakdown Spectroscopy (LIBS) is sufficiently high to enable said cathode composition to be suitable for use as a cathode electrode film in a lithium-ion battery.
61. The method of claim 45, wherein said cathode composition has an elasticity such that a calendared film of said composition can be formed into a tubular shape without fracture.
62. The method of claim 45, wherein said cathode active particles comprise lithium transition metal oxide.
63. The method of claim 45, wherein said tetrafluoroethylene polymer has a melt creep viscosity of at least about 1.8×10^{11} poise.

64. The method of claim 45, wherein said tetrafluoroethylene polymer has a melt creep viscosity of at least about 2.0×10^{11} poise.
65. The method of claim 45, wherein said tetrafluoroethylene polymer has a melt creep viscosity of at least about 3.0×10^{11} poise.
66. The method of claim 45, wherein said tetrafluoroethylene polymer has a melt creep viscosity of at least about 4.0×10^{11} poise.
67. The method of claim 45, wherein said elastomeric fluoropolymer has a Mooney viscosity of at least about 30 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.
68. The method of claim 45, wherein said elastomeric fluoropolymer has a Mooney viscosity of at least about 40 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.
69. The method of claim 45, wherein said elastomeric fluoropolymer has a Mooney viscosity of at least about 50 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.
70. The method of claim 45, wherein said elastomeric fluoropolymer has a Mooney viscosity of at least about 60 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.
71. The method of claim 45, wherein said elastomeric fluoropolymer has a Mooney viscosity of at least about 70 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.
72. The method of claim 45, wherein said elastomeric fluoropolymer is a vinylidene fluoride elastomeric fluoropolymer.
73. The method of claim 45, wherein said vinylidene fluoride elastomeric fluoropolymer comprises a vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene copolymer.

74. The method of claim 45, wherein said tetrafluoroethylene polymer is a tetrafluoroethylene homopolymer.
75. The method of claim 45, wherein said tetrafluoroethylene polymer is a tetrafluoroethylene homopolymer having a melt creep viscosity of at least about 4.0×10^{11} poise, and said elastomeric fluoropolymer is a vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene copolymer having Mooney viscosity of at least about 17 MU measured under conditions ML 1 + 10 (121°C) according to ASTM D1646.

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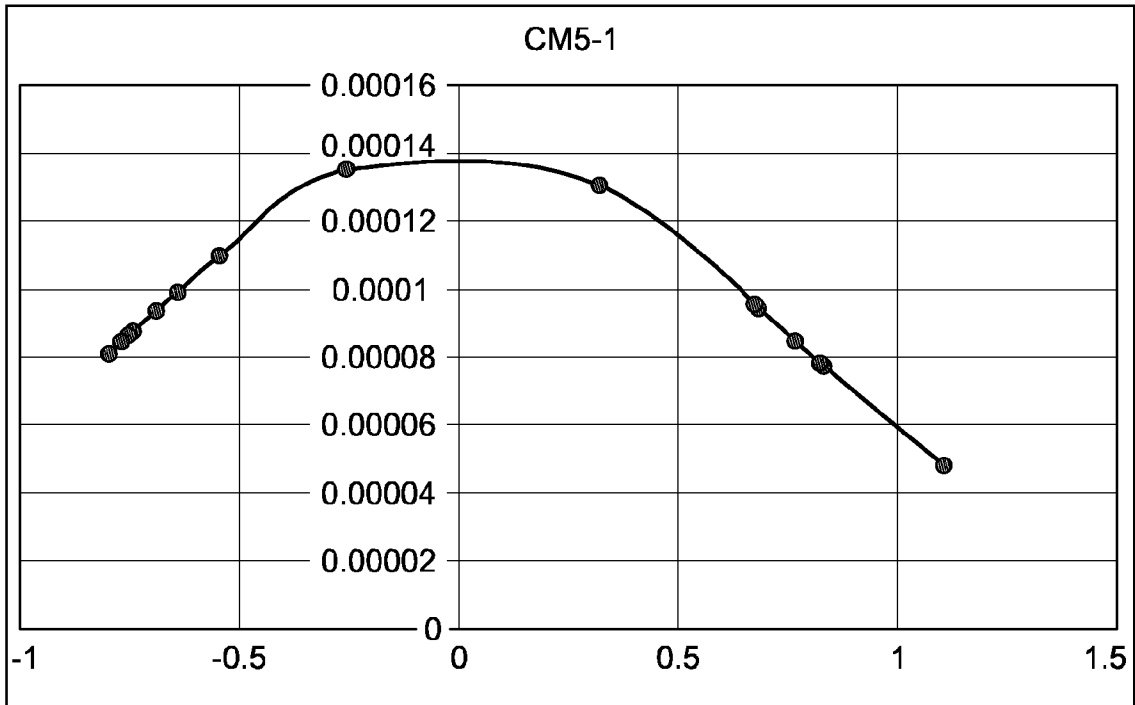


Figure 1

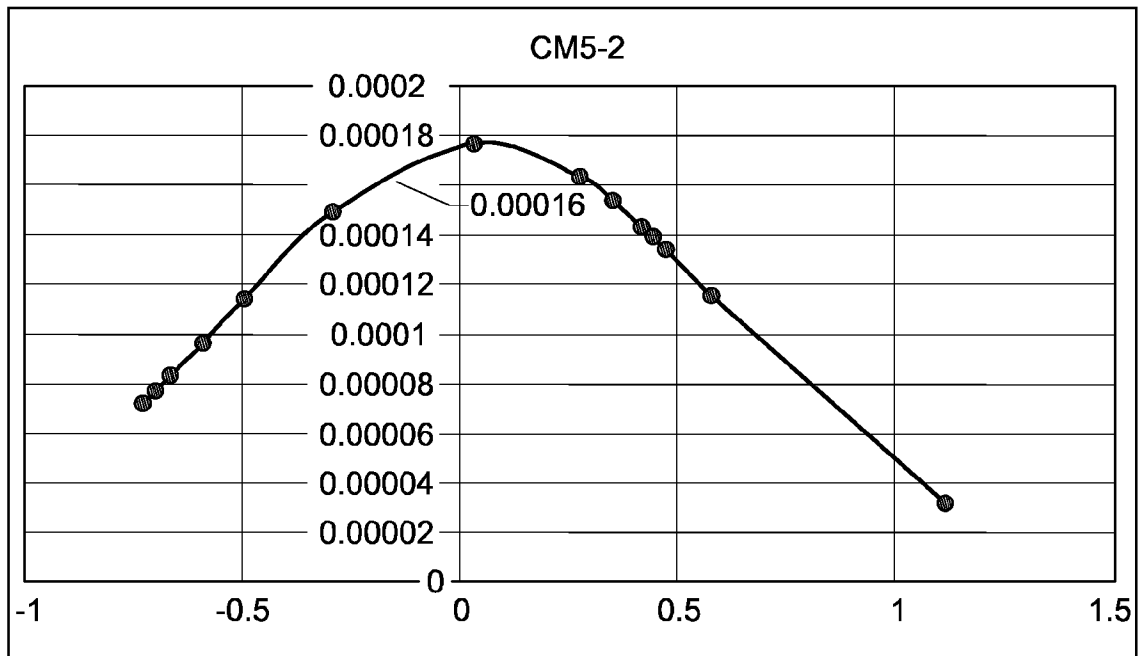


Figure 2

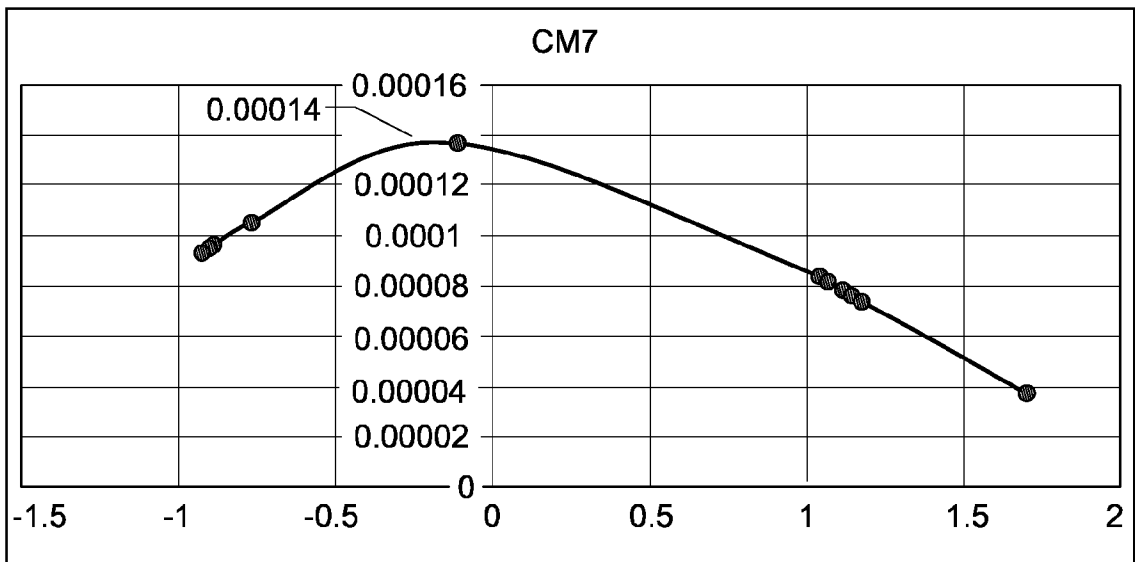


Figure 3

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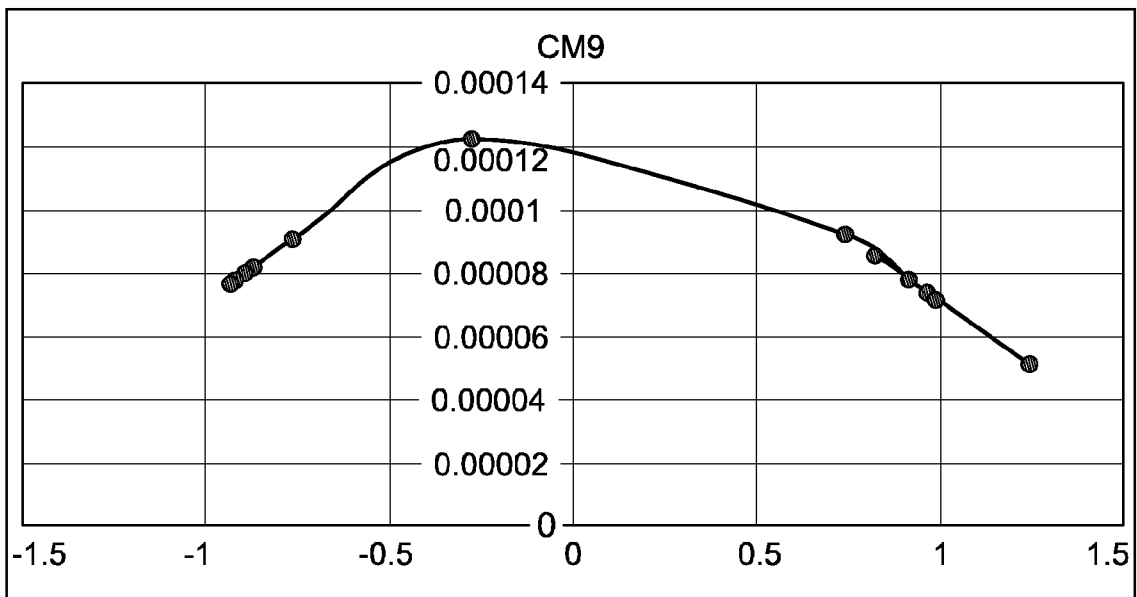


Figure 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2023/019220

A. CLASSIFICATION OF SUBJECT MATTER INV. H01M4/62 H01M4/04 H01M4/131 H01M4/1391 C08L27/16 C08L27/18 C08L27/20 ADD. H01M4/02 According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) H01M C09J C08L Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	US 2015/303481 A1 (DUONG HIEU MINH [US] ET AL) 22 October 2015 (2015-10-22) claim all -----	1-75		
X	US 2005/250908 A1 (BRIERS JORIS [BE] ET AL) 10 November 2005 (2005-11-10) paragraph [0042]; claim all -----	1-21		
A	WO 2021/127074 A1 (CHEMOURS CO FC LLC [US]) 24 June 2021 (2021-06-24) the whole document -----	22-75		
A	US 2021/098770 A1 (YUDI YUDI [US] ET AL) 1 April 2021 (2021-04-01) the whole document -----	1-75		
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.				
* Special categories of cited documents : <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 50%; border: none; vertical-align: top;"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family </td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family			
Date of the actual completion of the international search	Date of mailing of the international search report			
1 August 2023	08/08/2023			
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Götz, Heide			

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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