(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
30 January 2020 (30.01.2020)

WIPO | PCT

(10) International Publication Number
WO 2020/021530 A1

(51) International Patent Classification:
H01M 10/052 (2010.01) *H01M 10/0567* (2010.01)
H01M 10/0525 (2010.01) *H01M 10/0568* (2010.01)
H01M 10/0564 (2010.01) *H01M 10/0569* (2010.01)
H01M 10/0566 (2010.01) *H01M 6/16* (2006.01)

(21) International Application Number:
PCT/IL2019/050814

(22) International Filing Date:
21 July 2019 (21.07.2019)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
260745 23 July 2018 (23.07.2018) IL

(71) Applicant: **BAR-ILAN UNIVERSITY** [IL/IL]; 5290002 Ramat Gan (IL).

(72) Inventors: **LUSKI, Shalom**; 10/13 Alkali Street, 7630410 Rehovot (IL). **AURBACH, Doron**; 62 Uziel Street, 5164625 Bnei-Brak (IL). **YARIV, Ortal**; 2 Modeliani Street, 5951321 Bat Yam (IL).

(74) Agent: **LUZZATTO, Kfir** et al.; LUZZATTO & LUZZATTO, P.O. Box 5352, 8415202 Beer Sheva (IL).

(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, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, 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, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, 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, 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).

Declarations under Rule 4.17:
— *of inventorship (Rule 4.17(iv))*

Published:
— *with international search report (Art. 21(3))*

(54) Title: ELECTROLYTE SOLUTIONS FOR HIGH VOLTAGE LITHIUM-ION CELLS

(57) Abstract: The present invention relates to improved electrolyte solutions for rechargeable lithium-ion batteries based on fluorinated solvents, comprising at least one electrolyte and a solvent comprising at least two fluorinated alkyl carbonate. The improved electrolyte solution may also comprise at least one additive.

WO 2020/021530 A1

ELECTROLYTE SOLUTIONS FOR HIGH VOLTAGE LITHIUM-ION CELLS

FIELD OF THE INVENTION

The present invention relates to high voltage lithium-ion cells. More particularly, the invention relates to improved electrolyte solutions for rechargeable lithium-ion batteries based on fluorinated solvents.

BACKGROUND OF THE INVENTION

During recent years, the popularity of electric vehicles and hybrid electric vehicles has markedly increased worldwide. However, the main disadvantage of electric vehicles is the limited driving range, due to low battery capacity. Hence, there is an on-going demand for producing improved high voltage batteries, such as lithium-ion batteries (LIBs), in order to increase their capacity. Improving high voltage batteries by way of enhancing power or energy density may be carried out, for example, by developing improved high voltage cathode materials, such as high-energy nickel cobalt manganese oxide (HENCM) or lithium-manganese-rich (LMR) cathodes.

Nonetheless, there are several challenges which may prevent utilization of high voltage cathode materials, such as capacity fading over charge-discharge cycles, manganese dissolution from the cathode and compatibility of electrolyte solutions. In particular, conventional electrolyte solutions, which are based on alkyl carbonates, are highly subjected to decomposition at high potentials of 4.5 V and above, and are therefore not compatible with high voltage cells, which require operation voltage of about 4.6 – 4.8 versus Li/Li^+.

It is therefore an object of the present invention to provide an electrolyte solution compatible with high voltage batteries, having superior performances in terms of

enhanced stability, reduced manganese dissolution from the cathode and reduced capacity fading upon cycling.

It is another object of the invention to provide a Li-ion battery comprising the electrolyte solution presenting the above-mentioned advantages.

Other objects and advantages of the invention will become apparent as the description proceeds.

SUMMARY OF THE INVENTION

The present invention relates to an electrolyte solution comprising:

(a) at least one electrolyte;

(b) a solvent comprising at least two fluorinated alkyl carbonate; and optionally

(c) at least one additive.

The invention further relates to the electrolyte solution as described above wherein the electrolyte is $LiPF_6$ at a concentration of 1 M.

The invention additionally relates to the electrolyte solution according as described above, wherein the solvent is a combination of DMC, FEC and F-EPE (DMC:FEC:F-EPE) or a combination of DMC, F2EC and F-EPE (DMC:F2EC:F-EPE), at a volume ratio of 1:1:1.

The invention further relates to the electrolyte solution as described above, wherein the additive is TMSP, TMSPi or any combination thereof, wherein the total concentration of the additive in the electrolyte solution is 1 wt%.

Thus, the invention relates to an electrolyte solution, selected from the group consisting of:

- 1 M $LiPF_6$ in DMC:FEC:F-EPE at a volume ratio of 1:1:1;
- 1 M $LiPF_6$ in DMC:FEC:F-EPE at a volume ratio of 1:1:1 and 1 wt% TMSP;

- 1 M $LiPF_6$ in DMC:FEC:F-EPE at a volume ratio of 1:1:1 and 1 wt% TMSPi;
- 1 M $LiPF_6$ in DMC:F2EC:F-EPE at a volume ratio of 1:1:1;
- 1 M $LiPF_6$ in DMC:F2EC:F-EPE at a volume ratio of 1:1:1 and 1 wt% TMSP; and
- 1 M $LiPF_6$ in DMC:F2EC:F-EPE at a volume ratio of 1:1:1 and 1 wt% TMSPi.

The invention further relates to a battery comprising the electrolyte solutions as described above.

BRIEF DESCRIPTION OF THE DRAWINGS

Abbreviations used in the drawings: DMC (dimethyl carbonate); EC (ethylene carbonate); EMC (ethyl methyl carbonate); FEC (fluorinated ethylene carbonate); F2EC (2-fluorinated ethylene carbonate); F-EPE (1,1,2,2-tetrafluoroethyl 2,2,3,3,-tetrafluoropropyl ether); $LiPF_6$ (lithium hexaflurophosphate); TMSP (tris(trimethylsilyl)phosphate); TMSPi (tris(trimethylsilyl)phosphite).

Fig. 1 shows the temperature (T, °C) dependence of the specific conductivity (K, in millisiemens per meter) of the electrolyte solutions; a (1 M $LiPF_6$/DMC:EC:EMC, 3:3:3), b (1 M $LiPF_6$/DMC:FEC:F-EPE, 1:1:1), c (1 M $LiPF_6$/DMC:FEC:F-EPE, 1:1:1 + 1% TMSP), d (1 M $LiPF_6$/DMC:F2EC:F-EPE, 1:1:1), and e (1 M $LiPF_6$/DMC:F2EC:F-EPE, 1:1:1 + 1% TMSP).

Fig. 2 shows the current density (I) as a function of the cell's potential (E) during 5 cycles (C1–C5) of aluminum current collector, measured by cyclic voltammetry (at a scan rate of 1 mV/s) in 1 M $LiPF_6$/DMC:EC:EMC, 3:3:3 (a), 1 M $LiPF_6$/DMC:FEC:F-EPE, 1:1:1 + 1% TMSP (b) and 1 M $LiPF_6$/DMC:F2EC:F-EPE, 1:1:1 + 1% TMSP (c) solutions.

Fig. 3 shows the cycling performance of a Li/$Li_{1.2}Mn_{0.56}Co_{0.08}Ni_{0.16}O_2$ cell in 1 M $LiPF_6$/DMC:FEC:F-EPE, 1:1:1 electrolytes with and without 1% TMSP, between 3.0 and 4.7 V at a current rate of C/5.

Fig. 4A shows the cyclic stability of a $Li_{1.2}Mn_{0.56}Co_{0.08}Ni_{0.16}O_2$ cell in 1 M $LiPF_6$/DMC:EC:EMC, 3:3:3 (a), 1 M $LiPF_6$/DMC:FEC:F-EPE, 1:1:1 (b) and 1 M $LiPF_6$/DMC:F2EC:F-EPE, 1:1:1 (c) electrolyte solutions, between 3.0 and 4.7 V at a current rate of C/5.

Fig. 4B shows the cyclic stability of a $Li_{1.2}Mn_{0.56}Co_{0.08}Ni_{0.16}O_2$ cell in 1 M $LiPF_6$/DMC:FEC:F-EPE, 1:1:1 (a) 1 M $LiPF_6$/DMC:FEC:F-EPE, 1:1:1 + 1% TMSPi (b), 1 M $LiPF_6$/DMC:F2EC:F-EPE, 1:1:1 (c) and 1 M $LiPF_6$/DMC:F2EC:F-EPE, 1:1:1 + 1% TMSPi (d) electrolyte solutions, between 3.0 and 4.7 V at a current rate of C/5.

Fig. 5 shows the cyclic stability of a full cell ($Li_{1.2}Mn_{0.56}Co_{0.08}Ni_{0.16}O_2$ vs. graphite) in 1 M $LiPF_6$/DMC:FEC:DEC, 1:1:1 (a), 1 M $LiPF_6$/DMC:FEC:F-EPE, 1:1:1 + 1% TMSP (b), 1 M $LiPF_6$/DMC:F2EC:F-EPE, 1:1:1 (c) and 1 M $LiPF_6$/DMC:F2EC:F-EPE, 1:1:1 + 1% TMSP (d) electrolyte solutions, between 3.0 and 4.7 V at a current rate of C/5.

Fig. 6A shows the cyclic stability of a $Li_{1.2}Mn_{0.56}Co_{0.08}Ni_{0.16}O_2$ cell in 1 M $LiPF_6$/DMC:EC:EMC, 3:3:3 (a), 1 M $LiPF_6$/DMC:FEC:F-EPE, 1:1:1 (b), 1 M $LiPF_6$/DMC:FEC:F-EPE, 1:1:1 + 1% TMSPi (c) 1 M $LiPF_6$/DMC:F2EC:F-EPE, 1:1:1 (d) and 1 M $LiPF_6$/DMC:F2EC:F-EPE, 1:1:1 + 1% TMSPi (e) electrolyte solutions, between 3.0 and 4.7 V at a current rate of C/5; Fig. 6B shows the capacity retention of solutions a-e.

Fig. 7A shows the voltage profile during the first cycle of an $Li_{1.2}Mn_{0.56}Co_{0.08}Ni_{0.16}O_2$ cell in 1 M $LiPF_6$/DMC:EC:EMC, 3:3:3 (a), 1 M $LiPF_6$/DMC:FEC:F-EPE, 1:1:1 (b), 1 M $LiPF_6$/DMC:FEC:F-EPE, 1:1:1 + 1% TMSP (c) 1 M $LiPF_6$/DMC:F2EC:F-EPE, 1:1:1 (d) and 1 M $LiPF_6$/DMC:F2EC:F-EPE, 1:1:1 + 1% TMSPi (e) electrolyte solutions, between 3.0 and 4.7 V at a current rate of C/5; Fig. 7B shows the voltage profile during to 50^{th} cycle of $Li_{1.2}Mn_{0.56}Co_{0.08}Ni_{0.16}O_2$ cell in solutions a-e; Fig. 7C shows the voltage profile during to 100^{th} cycle of $Li_{1.2}Mn_{0.56}Co_{0.08}Ni_{0.16}O_2$ cell in solutions a-e.

Fig. 8A shows Nyquist impedance spectra plot of a $Li_{1.2}Mn_{0.56}Co_{0.08}Ni_{0.16}O_2$ cell in 1 M $LiPF_6$/DMC:EC:EMC, 3:3:3 (a), 1 M $LiPF_6$/DMC:FEC:F-EPE, 1:1:1 (b) and 1 M $LiPF_6$/DMC:FEC:F-EPE, 1:1:1 + 1% TMSP (c) electrolyte solutions recorded at 3.3 V during the 4^{th} cycle; Fig. 8B shows Nyquist impedance spectra plot of a $Li_{1.2}Mn_{0.56}Co_{0.08}Ni_{0.16}O_2$ cell in electrolyte solutions a-c recorded at 3.3 V during the 100^{th} cycle.

Fig. 9 shows high resolution scanning electron microscope (HRSEM) images of a pristine lithium-manganese-rich cathode (a) or after 100 cycles in 1 M $LiPF_6$/DMC:EC:EMC, 3:3:3 (b), 1 M $LiPF_6$/DMC:FEC:F-EPE, 1:1:1 (c), 1 M $LiPF_6$/DMC:FEC:F-EPE, 1:1:1 + 1% TMSP (d), 1 M $LiPF_6$/DMC:F2EC:F-EPE, 1:1:1 (e) and 1 M $LiPF_6$/DMC:F2EC:F-EPE, 1:1:1 + 1% TMSPi (f) electrolyte solutions.

DETAILED DESCRIPTION OF THE INVENTION

The electrolyte solution for high voltage lithium-ion cells according to the present invention addresses the need for an electrolyte solution which is compatible with high voltage batteries. The solution is thus a stable electrolyte solution, such that the components of the solution are less subject to decomposition at high voltage compared to components in conventional electrolyte solutions. Due to the increased stability of the components in the solution, capacity fading over multiple charge-discharge cycles of the battery is reduced. Moreover, the electrolyte solution described herein suppresses manganese dissolution from the cathode. Overall, the electrolyte solution of the invention enables the battery to maintain its functionality for a longer period of time compared to a battery employing conventional solutions.

The terms "conventional electrolyte solution" and "standard electrolyte solution" as used interchangeably herein refer to an electrolyte solution that is based on non-fluorinated alkyl carbonates as solvents, such as ethylene carbonate (EC), dimethyl carbonate (DMC) and/or ethyl methyl carbonate (EMC) solvents.

In one aspect of the invention, there is provided an electrolyte solution comprising:

(a) at least one electrolyte;

(b) a solvent comprising at least two fluorinated alkyl carbonates; and optionally

(c) at least one additive.

The term "electrolyte" as used herein refers to a substance (such as a soluble salt, acid or base), which produces an electrically conducting solution when dissolved in a polar solvent. The dissolved electrolyte dissociates into cations and anions, which disperse uniformly throughout the solvent. When an electric potential is applied to such a solution, the cations and anions of the solution are drawn to the oppositely charged electrode, thus producing a current.

According to a specific embodiment of the invention, the electrolyte is lithium hexaflurophosphate ($LiPF_6$) at a concentration of 1 M.

Fluorinated alkyl carbonates demonstrate higher oxidation potential compared to non-fluorinated alkyl carbonates, and are thus less subject to decomposition by oxidation at the operating voltage of the cell. The increased stability of fluorinated alkyl carbonates may be attributed to the strong electron-withdrawing effect of the fluorine atom. Due to their enhanced stability, electrolyte solutions based on fluorinated alkyl carbonates as solvents exhibit reduced irreversible capacity loss and consequently possess increased capacity retention. In other words, electrolyte solutions based on fluorinated alkyl carbonates as solvents maintain their discharge capacity upon a greater number of charge-discharge cycles of the battery when compared to conventional electrolyte solutions.

Furthermore, fluorinated alkyl carbonate solvents form a stable solid electrolyte interphase (SEI) film (i.e., passivation layer) on the surface of both the anode and the cathode. The performance of lithium-ion batteries depends greatly on the stability of

the SEI film formed on the surface of the negative electrode during the battery's first charge-discharge cycle. Hence, the use of fluorinated alkyl carbonates as solvents in the electrolyte solution improves the performance of the battery and increases its shelf life.

In some embodiments, the solvent in the electrolyte solution described herein comprises a combination of two fluorinated alkyl carbonates and one non-fluorinated alkyl carbonate.

The fluorinated alkyl carbonates used as solvents in the solution described herein is selected from the group consisting of fluorinated ethylene carbonate (FEC), 2-fluorinated ethylene carbonate (F2EC), and 1,1,2,2-tetrafluoroethyl 2,2,3,3,-tetrafluoropropyl ether (F-EPE).

In a specific embodiment, the solvent in the electrolyte solution described herein is a combination of DMC, FEC and F-EPE (DMC:FEC:F-EPE) or a combination of DMC, F2EC and F-EPE (DMC:F2EC:F-EPE), each at a volume ratio of 1:1:1.

The electrolyte solutions described herein may also comprise at least one additive.

In a specific embodiment of the invention, the additive is tris(trimethylesilyl) phosphate (TMSP), tris(trimethylsilyl) phosphite (TMSPi) or any combination thereof, wherein the total concentration of the additive in the electrolyte solution is 1 wt%. A non-limiting example of a combination of additives is a combination of 0.5% TMSP and 0.5% TMSPi.

The stability and performance of an electrolyte solution also depend on the presence of various impurities. For example, the presence of small amounts of water in the solution, leads to the formation of hydrofluoric acid (HF). The use of additives, such as TMSP and/or TMSPi, prevents the dissolution of Ni and Mn from the cathode, by removing the HF molecules that are present in the electrolyte solution.

By introducing additives into fluorinated electrolyte solutions, the cyclic stability of the cathode (e.g., $Li_{1.2}Mn_{0.56}Co_{0.08}Ni_{0.16}O_2$ cathode) is significantly enhanced. The improvement is attributed to the formation of a highly stable and protective SEI film on the cathode particles due to the preferential oxidation of the additives. Thus, the additives protect the cathode from degradation.

Moreover, the electrolyte solution comprising at least one additive exhibits increased discharge capacity and enhanced cycling performance due to the increased cathode stability and decreased electrolyte decomposition.

According to a specific embodiment of the invention, the electrolyte solution is selected from the group consisting of:

- 1 M $LiPF_6$ in DMC:FEC:F-EPE at a volume ratio of 1:1:1;
- 1 M $LiPF_6$ in DMC:FEC:F-EPE at a volume ratio of 1:1:1 and 1 wt% TMSP;
- 1 M $LiPF_6$ in DMC:FEC:F-EPE at a volume ratio of 1:1:1 and 1 wt% TMSPi;
- 1 M $LiPF_6$ in DMC:F2EC:F-EPE at a volume ratio of 1:1:1;
- 1 M $LiPF_6$ in DMC:F2EC:F-EPE at a volume ratio of 1:1:1 and 1 wt% TMSP; and
- 1 M $LiPF_6$ in DMC:F2EC:F-EPE at a volume ratio of 1:1:1 and 1 wt% TMSPi.

According to a further specific embodiment of the invention, the electrolyte solution comprises:

(a) 1 M $LiPF_6$;

(b) DMC:F2EC:F-EPE, at a volume ratio of 1:1:1; and

(c) 1 wt% TMSP.

This specific electrolyte solution provided in a HENCM Graphite cell (full lithium-ion cell) demonstrates breakthrough results regarding prevention of manganese dissolution

from the cathode and number of cycles. In particular, only 25% capacity fading was observed after 1000 charge-discharge cycles.

Thus, the extraordinary electrochemical stability of this electrolyte solution makes it a preferable candidate for other high voltage batteries.

In another aspect of the invention, there is provided a high voltage battery comprising the electrolyte solution described herein.

The battery comprising said electrolyte solution exhibits improved performance in terms of increased discharge capacity, enhanced cycling stability and safety.

The fluorinated alkyl carbonate solvents used in the electrolyte solution described herein exhibit lower flammability compared to their corresponding non-fluorinated carbonates. The non-flammability of the electrolyte solution renders the battery safe, for example, for transportation applications.

In one embodiment of the invention, the high voltage battery is a lithium-ion battery.

According to a specific embodiment of the invention, the lithium-ion battery is based on $Li_{1.2}Mn_{0.56}Co_{0.08}Ni_{0.16}O_2$ cathode.

The invention will now be described with reference to specific examples and materials. The following examples are representative of techniques employed by the inventors in carrying out aspects of the present invention. It should be appreciated that while these techniques are exemplary of specific embodiments for the practice of the invention, those of skill in the art, in light of the present disclosure, will recognize that numerous modifications can be made without departing from the spirit and intended scope of the invention.

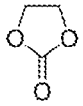
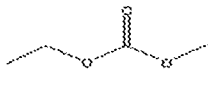
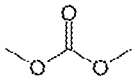
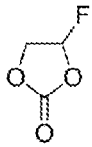
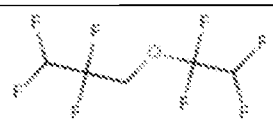
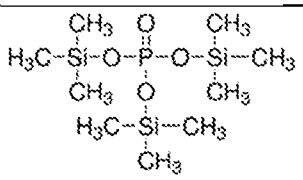
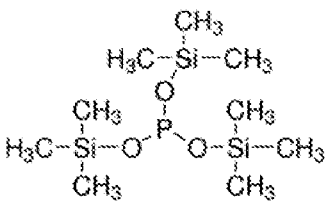
EXAMPLES

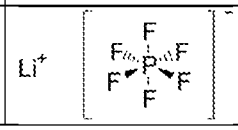
Materials and methods

Preparation of electrolyte solutions based on fluorinated solvents

Solvents, additives and salts used in the preparation of electrolyte solutions according to the inventions are shown in Table 1.

Table 1. Structural formulas of solvents, additives and salts

Name	Structural formula
Ethylene carbonate (EC)	
Ethyl methyl carbonate (EMC)	
Dimethyl carbonate (DMC)	
Fluorinated ethylene carbonate (FEC)	
2-fluorinated ethylene carbonate (F2EC)	
1,1,2,2-tetrafluoroethyl 2,2,3,3,-tetrafluoropropyl ether (F-EPE)	
Tris(trimethylsilyl)phosphate (TMSP)	
Tris(trimethylsilyl)phosphite (TMSPi)	

Name	Structural formula
Lithium hexafluorophosphate ($LiPF_6$)	

The following six different electrolyte solutions were prepared:

1. a mixture of DMC:FEC:F-EPE, 1:1:1 ratio by volume, containing 1 M $LiPF_6$;
2. a mixture of DMC:FEC:F-EPE, 1:1:1 ratio by volume, containing 1 M $LiPF_6$ with 1 wt% TMSP;
3. a mixture of DMC:FEC:F-EPE, 1:1:1 ratio by volume, containing 1 M $LiPF_6$ with 1 wt% TMSPi;
4. a mixture of DMC:F2EC:F-EPE, 1:1:1 ratio by volume, containing 1 M $LiPF_6$;
5. a mixture of DMC:F2EC:F-EPE, 1:1:1 ratio by volume, containing 1 M $LiPF_6$ with 1 wt% TMSP; and
6. a mixture of DMC:F2EC:F-EPE, 1:1:1 ratio by volume, containing 1 M $LiPF_6$ with 1 wt% TMSPi.

A mixture of DMC:EC:EMC, 3:3:3 ratio by weight, containing 1 M $LiPF_6$ was used as a standard electrolyte solution (reference solution).

Fabrication of cathodes electrodes and coin cells

Cathodes were made by mixing $Li_{1.2}Mn_{0.56}Co_{0.08}Ni_{0.16}O_2$ (HE5050, Tadiran) as an active material with super P-Li and polyvinylidene fluoride (PVDF) binder (86:6:8 by weight). The active material loading was approximately 10.3 mg/cm^2.

Coin cells (2325 coin cell parts from NRC, Canada) were fabricated in an argon filled glove-box (O_2 and water under 1 ppm) with a polypropylene separator (PP2500 Cellgard). Lithium foil (99.9% purity) was used as the counter electrode.

Electrochemical measurements

All the electrochemical measurements were performed at 30 ^{o}C in galvanostatic (constant current) mode experiments, using multi-channel computerized analyzers from Arbin and Maccor Inc, USA. The test voltage ranged from 3.0 to 4.8 V for the HENCM/Li cell.

The coin cells were cycled 4 formation cycles with a current rate of C/10 between 3.0 and 4.8 V, followed by 100 cycles at a rate of C/5 between 3.0 and 4.7 V.

Analytical measurements

A scanning electron microscope (SEM, FEI Company, Oregon) was used to image the morphologies of the electrodes before and after cycling. The contents of Mn and Ni deposited on Li foils were determined by inductively coupled plasma mass spectrometry (ICP-MS, U.S).

Example 1:

Fluorinated alkyl carbonates reduce conductivity of the electrolyte solution

The temperature dependence of the specific conductivity (κ) of the electrolyte solutions are shown in Fig. 1. The conductivity of $LiPF_6$/DMC:EC:EMC solution (curve a in Fig. 1) exhibits higher conductivity than that of $LiPF_6$/DMC:FEC:F-EPE solution (curve b in Fig. 1) in the temperature range of -28 ^{o}C to 60 ^{o}C. The replacement of FEC by F2EC (curve d in Fig. 1) decreases conductivity in the complete temperature range. The addition of TMSP to FEC and F2EC solutions (curves c and e in Fig. 1, respectively) has no effect on the conductivity of the solutions.

Example 2:

Addition of F-EPE as a third fluorinated solvent reduces current density

The anodic behavior of the aluminum current collector in different electrolyte solutions was investigated by cyclic voltammetry (CV) during 5 cycles. During the first cycle of the

cell, the native oxide layer on the aluminum is broken down, and the exposed aluminum reacts with fluorine to form a passivation layer of AlF_3 on the aluminum surface. As shown in Tables 2 and 3, as well as in Fig. 2, the first polarization cycle has very low current densities evolving above 3.5 V for all the tested solutions. These currents are associated with the degradation of the fluorinated solvents and the products forming a protective layer on the aluminum surface. In the following cycles, a negligible current flow was observed between 4.0 and 5.0 V. The peak observed at lower voltage is due to the breakdown of the native oxide layer on the aluminum. The results indicate that mixtures of electrolyte solutions that contain two fluorinated solvents and additives reduce the corrosion current of the aluminum compared to conventional solutions, due to the formation of a stable passivation layer on the aluminum surface. The formation of a stable passivation layer enables better performances and longer shelf life of the battery.

Table 2. Current density of 5 electrolyte solutions at a cell's potential of 4.5 V during 5 cycles

Electrolyte solution	**Cycle 1**	**Cycle 3**	**Cycle 5**
$LiPF_6$/DMC:EC:EMC	0.0029	0.0000626	0.0000403
$LiPF_6$/DMC:FEC:F-EPE	0.0022	0.0000421	0.0000279
$LiPF_6$/DMC:F2EC:F-EPE	0.0026	0.0000526	0.0000347
$LiPF_6$/DMC:FEC:F-EPE + 1% TMSP	0.0023	0.0000374	0.0000259
$LiPF_6$/DMC:F2EC:F-EPE + 1% TMSP	0.0024	0.0000257	0.0000174

Table 3. Current density of 5 electrolyte solutions at a cell's potential of 5 V during 5 cycles

Electrolyte solution	**Cycle 1**	**Cycle 3**	**Cycle 5**
$LiPF_6$/DMC:EC:EMC	0.003	0.0000287	0.000212
$LiPF_6$/ DMC:FEC:F-EPE	0.0024	0.000115	0.0000732
$LiPF_6$/DMC:F2EC:F-EPE	0.0027	0.000139	0.0000849

Electrolyte solution	Cycle 1	Cycle 3	Cycle 5
$LiPF_6$/DMC:FEC:F-EPE + 1% TMSP	0.0027	0.000136	0.0000866
$LiPF_6$/DMC:F2EC:F-EPE + 1% TMSP	0.0026	0.0000807	0.0000481

Example 3:

Addition of TMSP improves cycling performance of lithium-ion batteries in coin cell

The cycling performance of $Li/Li_{1.2}Mn_{0.56}Co_{0.08}Ni_{0.16}O_2$ cells containing the electrolytes 1 M $LiPF_6$ in DMC:FECF-EPE (1:1:1 by volume) with and without 1% TMSP is shown in Fig. 3. All the cells with different electrolytes were first subjected to four formation cycles with a current rate of C/10. The following cycles were cycled at a current rate of C/5. At the fifth cycle, the discharge capacity of the cell without TMSP was 224 mAh/gr and the discharge capacity of the cell with TMSP was 274 mAh/gr. Moreover, at the 100th cycle, the residual discharge capacities were 195 mAh/gr for the electrolyte without TMSP and 249 mAh/gr for the electrolyte with 1% TMSP. The capacity retentions at the 100th cycle were 79.9% without TMSP and 91.1% for 1% TMSP. As compared with the electrolyte without TMSP, the cycling performance of the cell containing 1% TMSP is improved, at lease because the presence of TMSP stabilizes the interphase between $Li_{1.2}Mn_{0.56}Ni_{0.13}Co_{0.08}Ni_{0.16}O_2$ cathode and electrolyte.

Example 4:

F2EC-based electrolytes improves anodic stability

The cycling performance of $Li/Li_{1.2}Mn_{0.56}Co_{0.08}Ni_{0.16}O_2$ cells with FEC- and F2EC-based electrolyte solutions is shown in Figs. 4A and 4B. Higher capacity retention and lower irreversible capacity loss were observed for the cells cycled with the F2EC-based electrolyte solution compared to those of cells cycled with the FEC-based solution. The F2EC-based solution had higher anodic stability compared to that of the FEC-based electrolyte.

Fig. 5 shows the cyclic stability of full cell ($Li_{1.2}Mn_{0.56}Co_{0.08}Ni_{0.16}O_2$ vs. graphite) in FEC- and F2EC-based electrolytes with and without 1% TMSP. When TMSP was added to the electrolytes, the cycling stability of the cathode after 600 cycles was significantly improved.

Example 5:

Fluorinated electrolyte solution in the presence of an additive improves cycling performance of lithium-ion batteries

As shown in Fig. 6A, when TMSPi was added to the F2EC-based electrolyte solutions, the cycling stability of the cathode was significantly enhanced. Fig. 6B shows that the capacity retention after 100 cycles of DMC:F2EC:F-EPE + 1% TMSPi solution was enhanced to 96.7%, suggesting that the electrolyte decomposition was suppressed by using TMSPI. Addition of TMSPi to the FEC-based electrolyte solutions also significantly enhances the cycling stability of the cathode (Fig. 6A). The capacity retention after 100 cycles of DMC:FEC:F-EPE solution was enhanced compared to non-fluorinated electrolytes to 79.9%, while addition of 1% TMSPi further enhanced the capacity retention to 91.06%. These results indicate that a protective solid electrolyte interface (SEI) film is formed due to the preferential oxidation of TMSPi. Subsequently, the SEI film suppresses the successive electrolyte decomposition and protects $Li_{1.2}Mn_{0.56}Co_{0.08}Ni_{0.16}O_2$ from degradation.

Figs. 7A-7C describe the discharge voltage profiles of $Li_{1.2}Mn_{0.56}Co_{0.08}Ni_{0.16}O_2$ cell (vs lithium) in FEC- and F2EC- based electrolytes compared to standard electrolyte solution, between 3.0 and 4.7V at C/5. During the first cycle (Fig. 7A) the discharge voltage profiles are similar for all tested solutions. No significate changes were observed in the 50^{th} cycle (Fig. 7B). However, after 100 cycles (Fig. 7C), the discharge voltage profile degraded severely while using conventional alkyl carbonate solution (EC: EMC: DMC) in contrast to electrolyte solutions which contain fluorinated alkyl carbonates. The results are in accordance with the inferior electrochemical stability of non-fluorinated alkyl

carbonates, such as EC (ethylene carbonate), EMC (ethyl methyl carbonate) and DMC (dimethyl carbonate) compared to fluorinated alkyl carbonates.

Inductively coupled plasma mass spectrometry (ICP-MS) was carried out to further analyze the chemical composition of the slurry on the lithium metallic anode after cycling for 100 cycles. The two lithium electrodes cycled in each of the tested electrolyte solutions were first dissolved in 10 ml deionized water. The content of Co, Mn and Ni in the deionized water was then investigated. As shown in Table 4, the content of Mn was 0.01 μg per 1 mg of active material of the electrode (AM) for the FEC-based electrolyte solution without TMSP. The content of Mn for the FEC-based electrolyte solution with 1 wt% TMSP was 0.013 μg per 1 mg of AM. The content of Mn was 0.004 μg per 1 mg of AM for the F2EC-based electrolyte solution without TMSP, and 0.007 μg per 1 mg of AM for the F2EC-based electrolyte solution with 1 wt% TMSP. The content of Mn for the conventional electrolyte solution (DMC:EC:EMC) was 0.18 ppm. These results indicate that TMSP prevents the dissolution of Mn and Ni from the cathode by removing HF molecules from the electrolyte at a high charge potential of 4.8 V. Moreover, the use of electrolyte solutions based on fluorinated solvents compared the conventional electrolyte solution also prevents dissolution of Mn and Ni from the cathode.

Table 4. Mn, Co and Ni content in 10 ml deionized water after 100 cycles of lithium electrodes

Electrolyte solution	**Co 228.616 (μg per 1 mg of AM)**	**Mn 257.611 (μg per 1 mg of AM)**	**Ni 221.648 (μg per 1 mg of AM)**
DMC:EC:EMC	0.04	0.18	0.1
DMC:FEC:F-EPE	0.0015	0.01	0.007
DMC:FEC:F-EPE + 1% TMSPi	ND	0.01	0.005
DMC:FEC:F-EPE + 1% TMSP	0.0015	0.013	0.006
DMC:F2EC:F-EPE	ND	0.007	ND

Electrolyte solution	Co 228.616 (µg per 1 mg of AM)	Mn 257.611 (µg per 1 mg of AM)	Ni 221.648 (µg per 1 mg of AM)
DMC:F2EC:F-EPE + 1% TMSPi	ND	0.007	ND
DMC:F2EC:F-EPE + 1% TMSP	ND	0.004	ND

In order to understand the effect of electrolyte additives, electrochemical impedance spectra (EIS) of Li/HENCM cells were recorded at an open circuit voltage (OCV) of 3.3 V during the 4^{th} and 100^{th} cycle with an alternating current amplitude of 5 mV in the frequency range of between 100 kHz and 0.01 Hz in FEC-based electrolyte solution with or without 1% TMSP compared to the conventional solution. The Nyquist impedance spectra plot of HENCM cells in the FEC-based electrolyte with or without 1% TMSP consist of two semicicrcles in the 4^{th} cycle (Fig. 8A) and a broad semicircle in the 100^{th} cycle at the high frequency region followed by a linear spike at the low frequency region (Fig. 8B). As shown in Fig. 8B, the curve is composed of two overlapping semicircles in the high-to-medium frequency range and a straight line in the low frequency range. The semicircle of the SEI film resistance in the high frequency range is attributed to Li ion migration through the interphase film between the electrode and the electrolyte, while the semicircle in the medium frequency range is assigned to charge transfer resistance. Fig. 8A clearly shows that the cell containing 1% TMSP exhibits a higher interphase resistance than the cell without TMSP during the 4^{th} cycle, suggesting that an interphase film with high resistance was formed on the surface of the high-voltage $Li_{1.2}Mn_{0.56}Co_{0.08}Ni_{0.16}O_2$ cathode. On the contrary, the Nyquist plot for the 100^{th} cycle shown in Fig. 8B consists of a broad semicircle due to combination of the capacitive and resistive elements of the cell. The cell without TMSP shows a higher interphase resistance than the cell with 1% TMSP during the 100^{th} cycle, even though the resistance of both cells had increased.

The scanning electron microscope (SEM) images of the cathodes after 100 cycles in the fluorinated-based electrolyte solutions with or without TMSP or TMSPi additives, compared to the pristine electrode and conventional electrolyte solution are shown in Fig. 9. While the pristine cathode shows clean HENCM crystals and a carbon black network in between, the cycled cathode using fluorinated-based electrolyte solution without an additive shows a thick surface film on the Li-Mn-rich (LMR) particles as well as on the carbon black network. By contrast, the cycled cathode using fluorinated-based electrolyte solutions with an additive seems almost as clean as the pristine cathode. These results clearly demonstrate the stability of TMSP against oxidation on the cathode surface. Moreover, high resolution SEM (HRSEM) images of the HENCM electrode cycled in the conventional electrolyte solution provide clear visual evidence for the mechanism of their capacity fading.

CLAIMS

1. An electrolyte solution comprising:
   (a) at least one electrolyte;
   (b) a solvent comprising at least two fluorinated alkyl carbonate; and optionally
   (c) at least one additive.

2. The electrolyte solution according to claim 1, wherein the electrolyte is $LiPF_6$ at a concentration of 1 M.

3. The electrolyte solution according to claim 1 or 2, wherein the solvent is a combination of DMC, FEC and F-EPE (DMC:FEC:F-EPE) or a combination of DMC, F2EC and F-EPE (DMC:F2EC:F-EPE), at a volume ratio of 1:1:1.

4. The electrolyte solution according to any one of claims 1-3, wherein the additive is TMSP, TMSPi or any combination thereof, wherein the total concentration of the additive in the electrolyte solution is 1 wt%.

5. The electrolyte solution according to claim 1, selected from the group consisting of:
   - 1 M $LiPF_6$ in DMC:FEC:F-EPE at a volume ratio of 1:1:1;
   - 1 M $LiPF_6$ in DMC:FEC:F-EPE at a volume ratio of 1:1:1 and 1 wt% TMSP;
   - 1 M $LiPF_6$ in DMC:FEC:F-EPE at a volume ratio of 1:1:1 and 1 wt% TMSPi;
   - 1 M $LiPF_6$ in DMC:F2EC:F-EPE at a volume ratio of 1:1:1;
   - 1 M $LiPF_6$ in DMC:F2EC:F-EPE at a volume ratio of 1:1:1 and 1 wt% TMSP; and
   - 1 M $LiPF_6$ in DMC:F2EC:F-EPE at a volume ratio of 1:1:1 and 1 wt% TMSPi.

6. A battery comprising the electrolyte solution according to any one of claims 1-5.

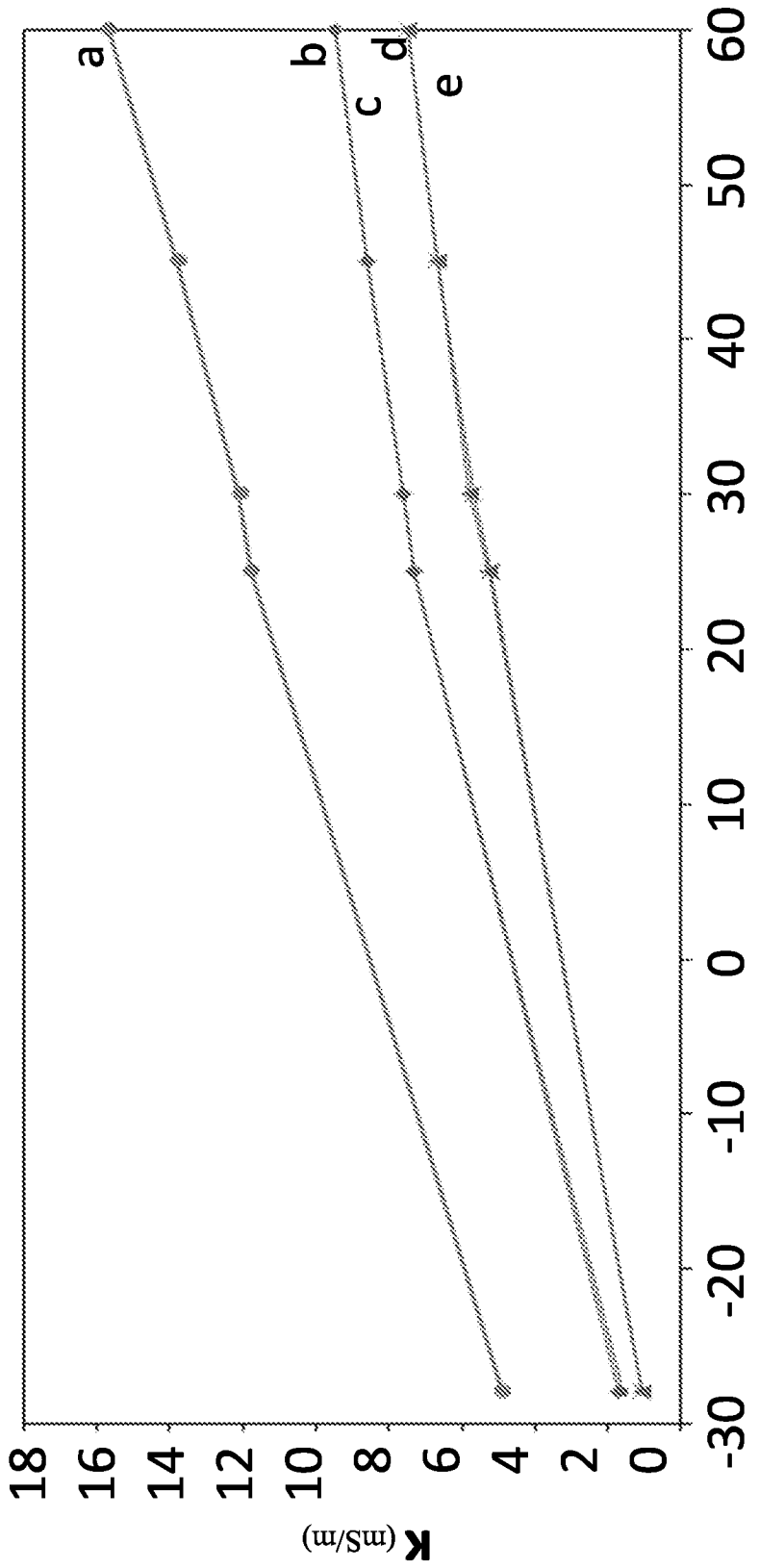


Fig. 1

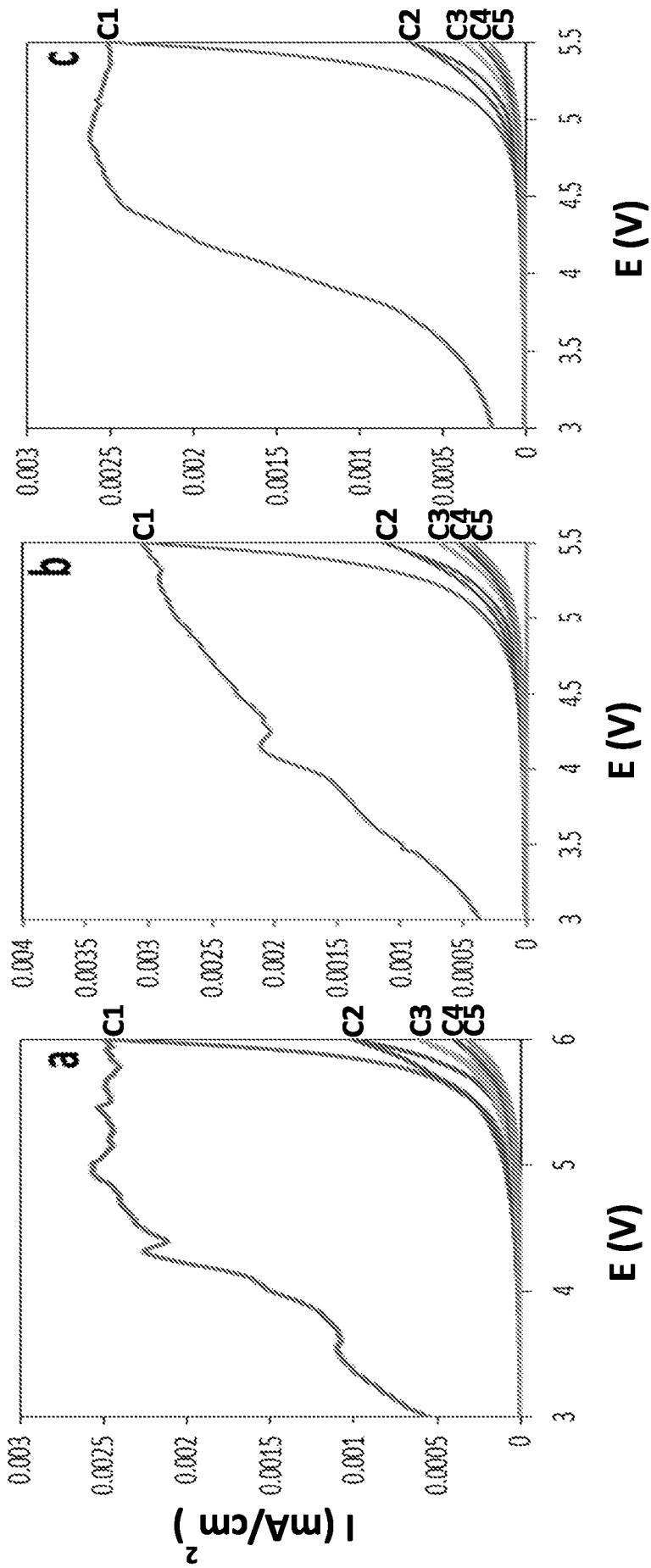

a
b
c
C1
C2
C3
C4
C5
i (mA/cm²)
E (V)
0.003
0.0025
0.002
0.0015
0.001
0.0005
0.004
0.0035
0
3
4
5
6
3.5
4.5
5.5

Fig. 2

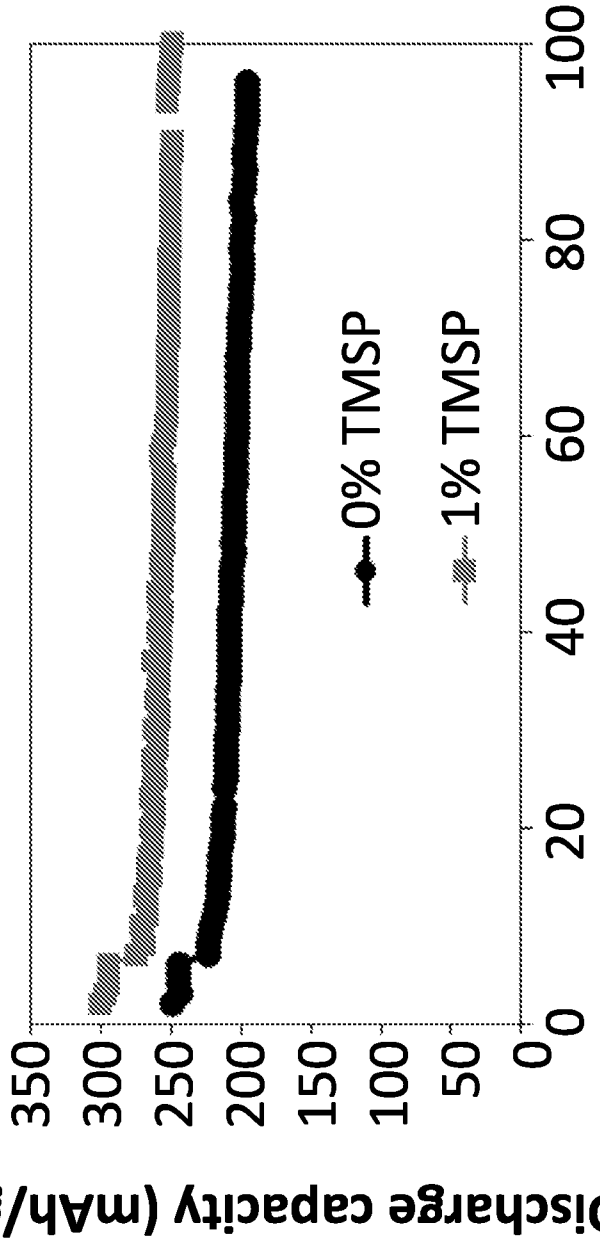

Discharge capacity (mAh/g)
350
300
250
200
150
100
50
0
0
20
40
60
80
100
Cycle
0% TMSP
1% TMSP

Fig. 3

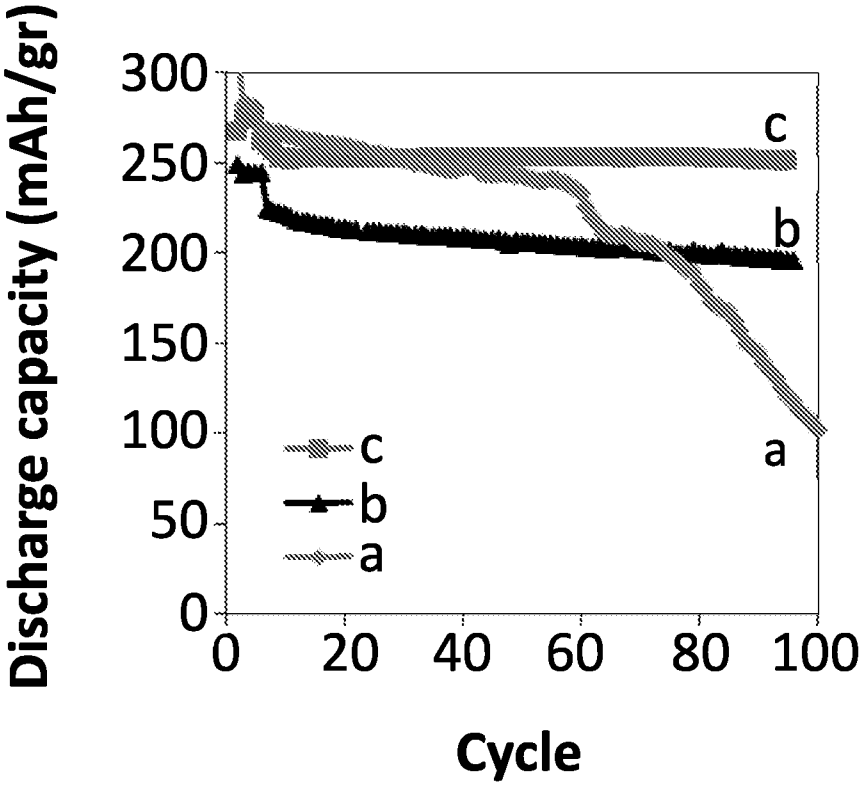

Discharge capacity (mAh/gr)
300
250
200
150
100
50
0
0
20
40
60
80
100
Cycle
c
b
a
c
b
a

Fig. 4A

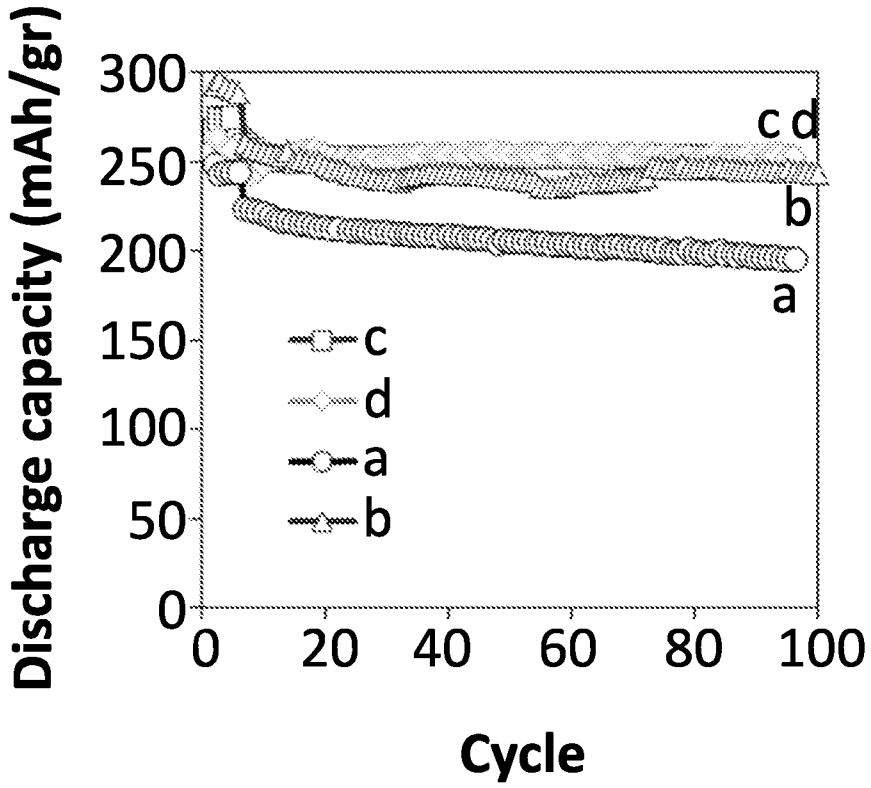

Discharge capacity (mAh/gr)
300
250
200
150
100
50
0
0
20
40
60
80
100
Cycle
c d
b
a
c
d
a
b

Fig. 4B

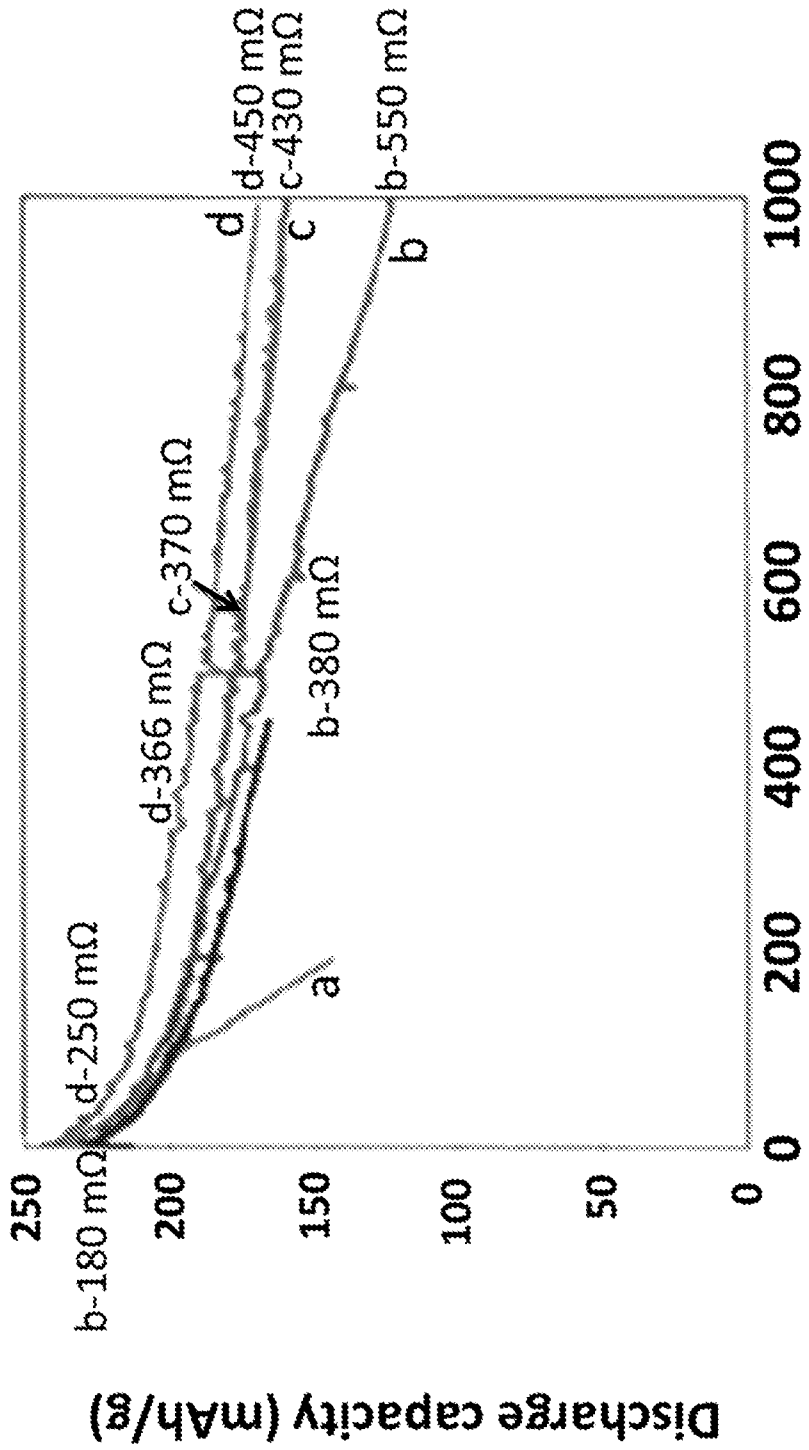

Discharge capacity (mAh/g)
250
200
150
100
50
0
0
200
400
600
800
1000
Cycle
b-180 mΩ
d-250 mΩ
d-366 mΩ
c-370 mΩ
b-380 mΩ
d-450 mΩ
c-430 mΩ
b-550 mΩ
a
b
c
d

Fig. 5

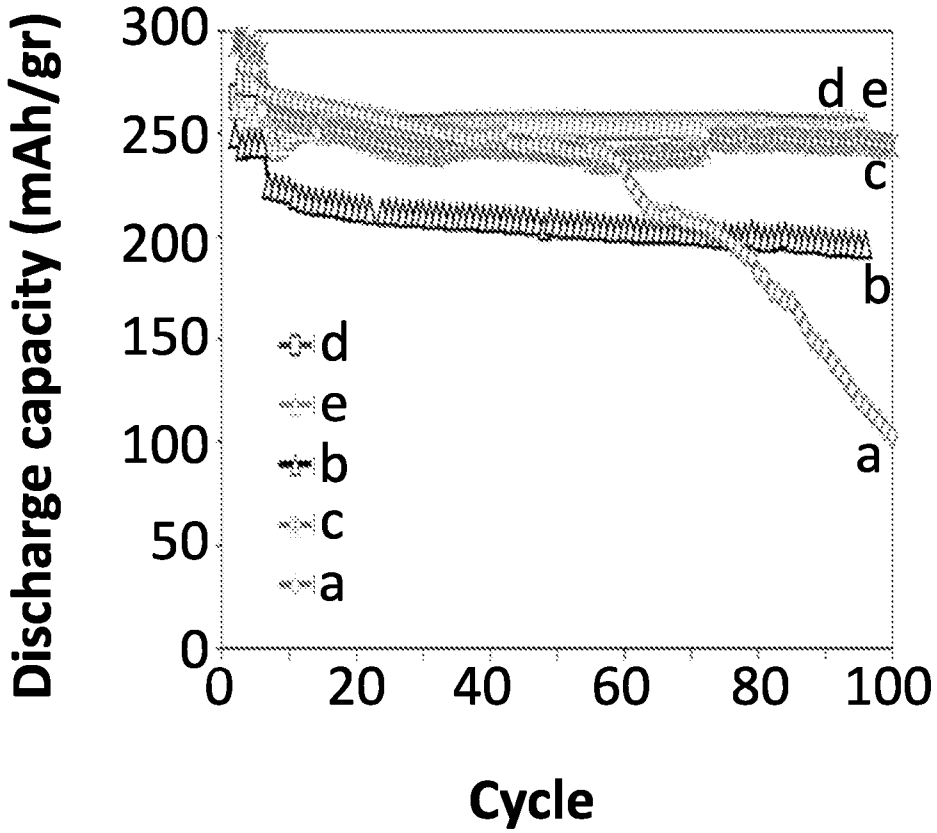

Discharge capacity (mAh/gr)
300
250
200
150
100
50
0
0
20
40
60
80
100
Cycle
d
e
b
c
a
d e
c
b
a

Fig. 6A

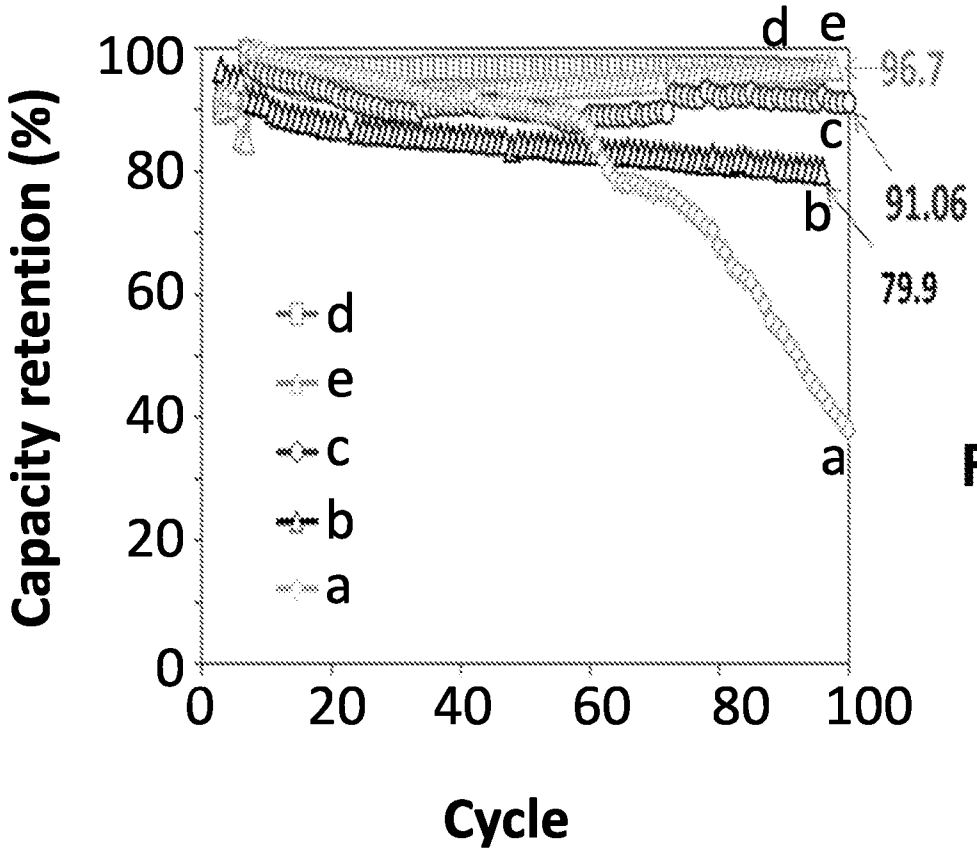

Capacity retention (%)
100
80
60
40
20
0
0
20
40
60
80
100
Cycle
d
e
c
b
a
d e
96.7
c
91.06
b
79.9
a

Fig. 6B

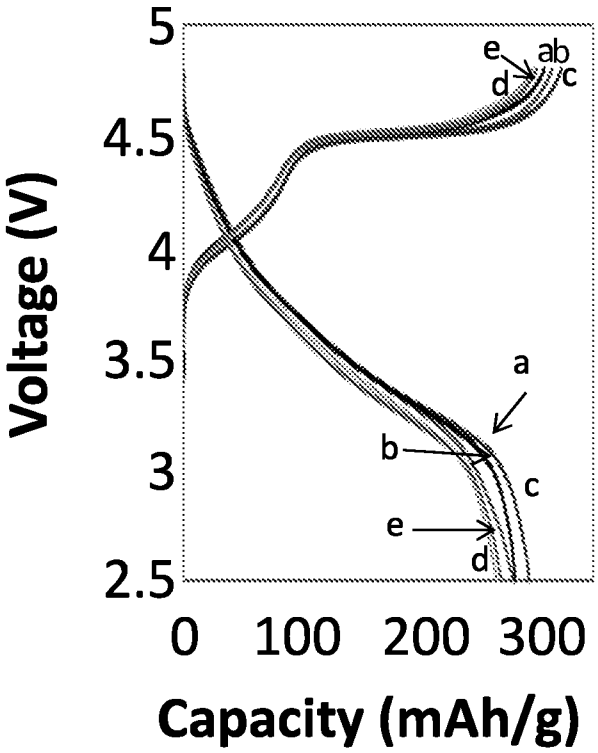

5
4.5
4
3.5
3
2.5
Voltage (V)
0
100
200
300
Capacity (mAh/g)
e
ab
d
c
a
b
c
e
d

Fig. 7A

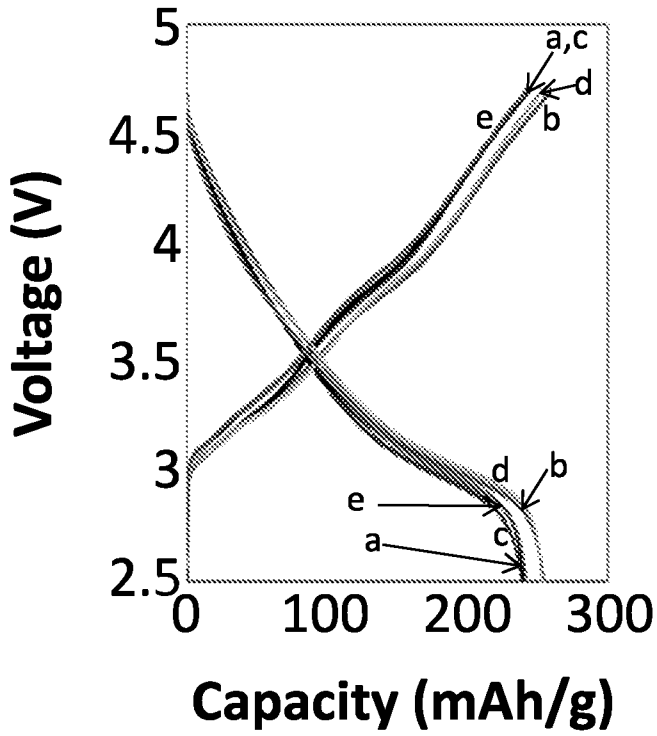

5
4.5
4
3.5
3
2.5
Voltage (V)
0
100
200
300
Capacity (mAh/g)
a,c
d
e
b
d
b
e
c
a

Fig. 7B

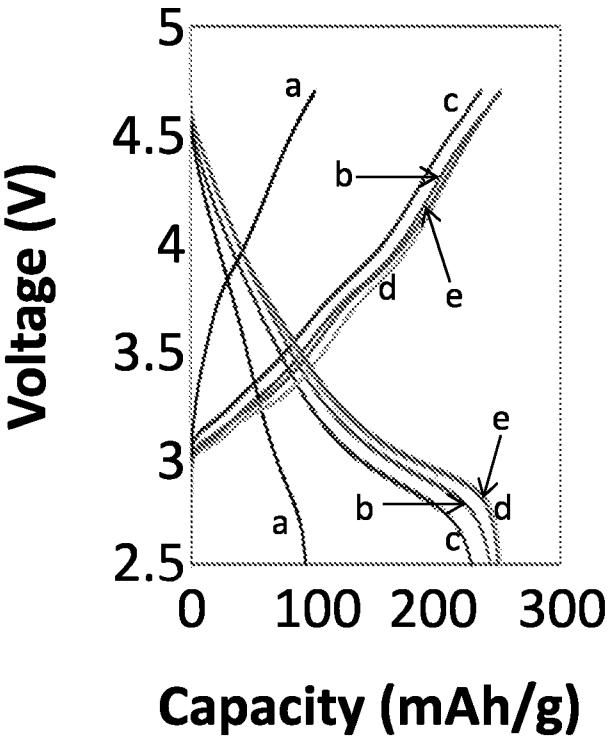


Fig. 7C

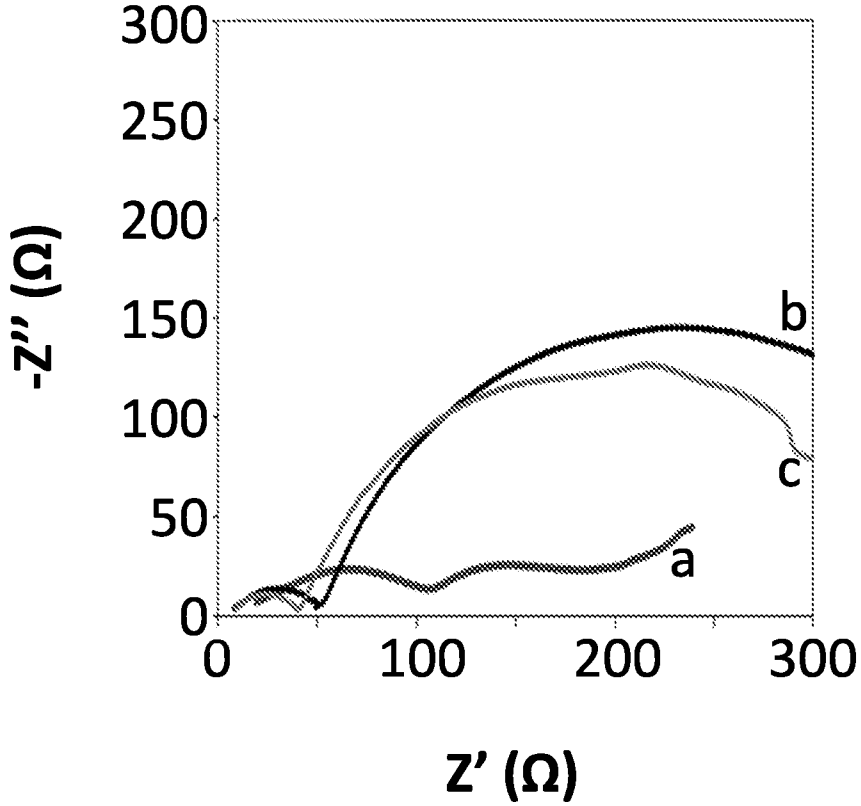

300
250
200
150
100
50
0
-Z'' (Ω)
0
100
200
300
Z' (Ω)
a
b
c

Fig. 8A

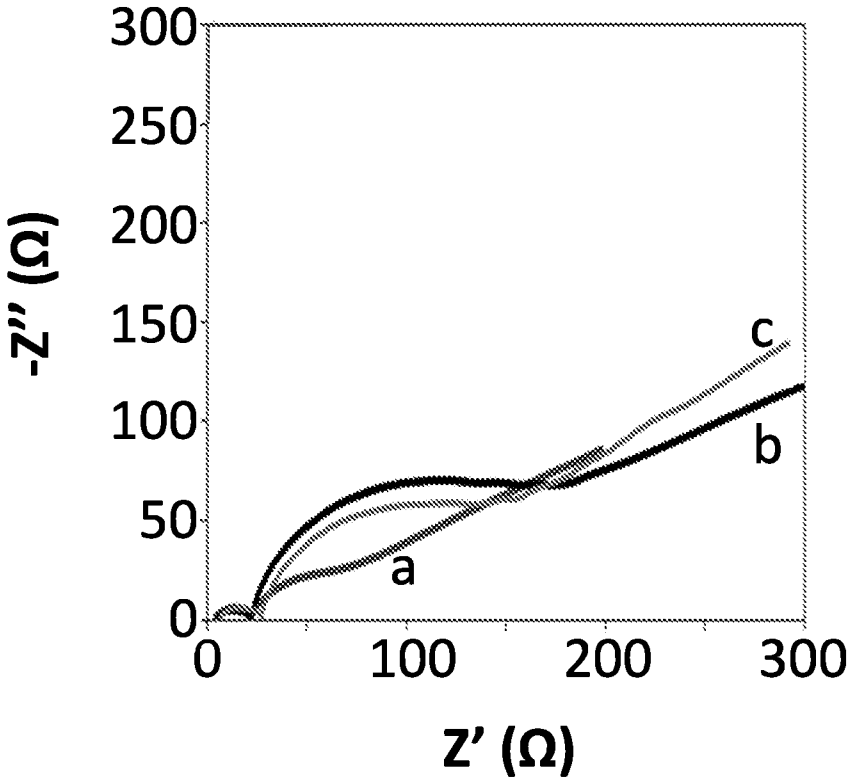

300
250
200
150
100
50
0
-Z'' (Ω)
0
100
200
300
Z' (Ω)
a
b
c

Fig. 8B

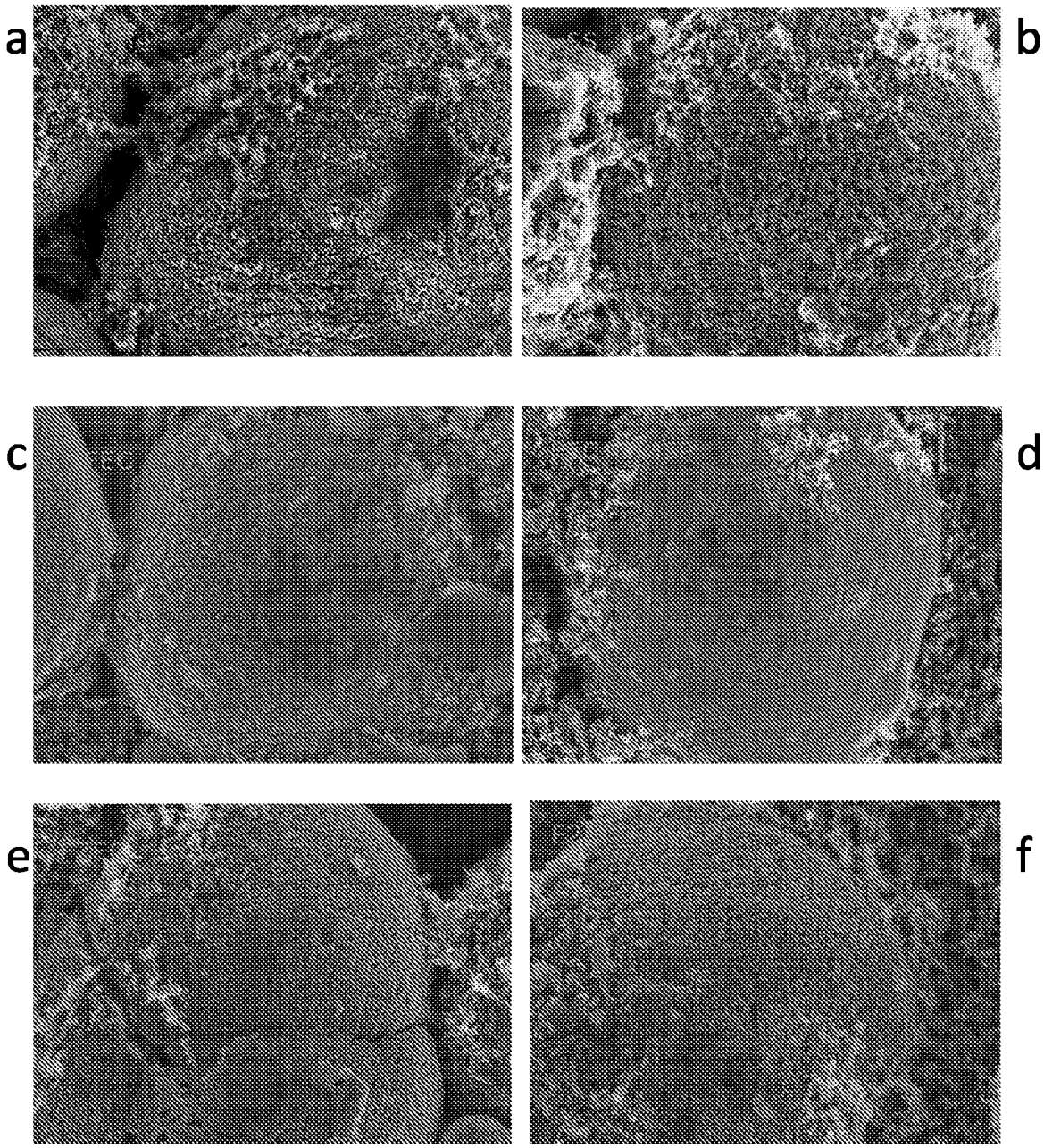


Fig. 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IL2019/050814

A. CLASSIFICATION OF SUBJECT MATTER
See extra sheet.

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)
IPC (20190101) H01M 10/052, H01M 10/0525, H01M 10/0564, H01M 10/0566, H01M 10/0567, H01M 10/0568, H01M 10/0569, H01M 6/16
CPC (20130101) H01M 10/052, H01M 10/0525, H01M 10/0564, H01M 10/0566, H01M 10/0567, H01M 10/0568, H01M 10/0569, H01M 6/16

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)
Databases consulted: Google Patents, Google Scholar, Orbit
Search terms used: Fluoroethylene carbonate ,fluorinated ether , electrolyte,FEC , F2EC, battery

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Synergistic Effect of Partially Fluorinated Ether and Fluoroethylene Carbonate for High-Voltage Lithium-Ion Batteries with Rapid Chargeability and Dischargeability, ACS Appl. Mater. Interfaces, 9 (50), 44161-44172, 2017-11-28 (https://doi.org/10.1021/acsami.7b12352) Choon-Ki Kim et al 28 Nov 2017 (2017/11/28) p 44162, c 1, section 2.1	3
Y	p 44162, c 1, section 2.1	4-6
Y	US 7494746 B2 SAMSUNG SDI CO., LTD 24 Feb 2009 (2009/02/24) c 10, table 1 and examples 3-4,	4-6
X	US 2014302401 A1 DU PONT [US] 10 Sep 2019 (2019/09/10) [0009], [0011],[0092],[0097]	1,2,6

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"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
23 Sep 2019	24 Sep 2019
Name and mailing address of the ISA: Israel Patent Office Technology Park, Bldg.5, Malcha, Jerusalem, 9695101, Israel Facsimile No. pctoffice@justice.gov.il	Authorized officer BERKOWITZ Tzipora Telephone No. 972-73-3927259

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IL2019/050814

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2016118690 A1 SOLVAY FLUOR GMBH[DE]; WESTF LISCHE WILHELMS UNIVERSIT T M?NSTER [DE]; INST POLYTECHNIQUE GRENOBLE [FR]; CENTRE NAT RECH SCIENT [FR] 28 Apr 2016 (2016/04/28) whole document	1-6

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IL2019/050814

Patent document cited search report	Publication date	Patent family member(s)	Publication Date
US 7494746 B2	24 Feb 2009	US 2008118843 A1	22 May 2008
		US 7494746 B2	24 Feb 2009
		CN 101188313 A	28 May 2008
		CN 101188313 B	29 Dec 2010
		EP 1926172 A1	28 May 2008
		JP 2008130544 A	05 Jun 2008
		KR 100804696 B1	18 Feb 2008
US 2014302401 A1	10 Sep 2019	US 2014302401 A1	09 Oct 2014
		CA 2908044 A1	09 Oct 2014
		CN 105556729 A	04 May 2016
		CN 105556729 B	09 Apr 2019
		EP 2982002 A1	10 Feb 2016
		EP 2982002 B1	17 Jul 2019
		JP 2016519400 A	30 Jun 2016
		KR 20150138326 A	09 Dec 2015
		US 2014302402 A1	09 Oct 2014
		WO 2014165748 A1	09 Oct 2014
US 2016118690 A1	28 Apr 2016	US 2016118690 A1	28 Apr 2016
		CA 2911079 A1	06 Nov 2014
		EP 2800197 A1	05 Nov 2014
		EP 2800197 B1	22 Mar 2017
		JP 2016532237 A	13 Oct 2016
		WO 2014177702 A1	06 Nov 2014
		WO 2014177704 A1	06 Nov 2014

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IL2019/050814

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (20190101) H01M 10/052, H01M 10/0525, H01M 10/0564, H01M 10/0566, H01M 10/0567, H01M 10/0568, H01M 10/0569, H01M 6/16

CPC (20130101) H01M 10/052, H01M 10/0525, H01M 10/0564, H01M 10/0566, H01M 10/0567, H01M 10/0568, H01M 10/0569, H01M 6/16