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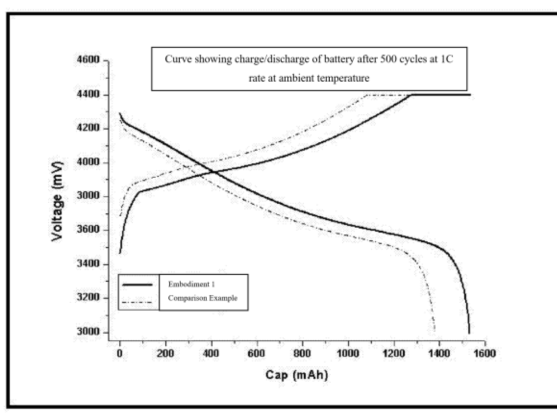
Claims 1 page Description 6 pages Drawings 1 page

(54) Title of Invention: Wide-temperature-range homogeneous non-aqueous electrolyte solution

(57) Abstract

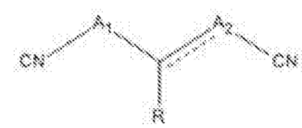
Disclosed is a wide-temperature-range homogeneous non-aqueous electrolyte solution containing a non-aqueous organic solvent, electrolyte lithium salt, and additive combination; said non-aqueous organic solvent is an optimized and combined multi-component homogeneous mixed solvent; said additive combination can effectively protect the structural stability of positive and negative electrode materials, and has excellent solubility in the mixed solvent. The components of the non-aqueous electrolyte solution of the present invention have a suitable ratio and are highly soluble with each other, and the homogeneous and stable mixed solution state can be maintained even after storage for a long period of time in an environment below -30°C, solving the problem that conventional high-voltage non-aqueous electrolyte solutions tend to precipitate crystals at low temperatures and facilitating the transportation and long-term storage of the non-aqueous electrolyte solution in the north of China; the electrolyte solution is also highly wettable to the electrode material, has good electrode interfacial compatibility, ensuring good high-voltage performance of a lithium-ion battery.



1. A wide-temperature-range homogeneous non-aqueous electrolyte solution containing a non-aqueous organic solvent, electrolyte lithium salt, and additive combination; characterized in that: said non-aqueous organic solvent is the following multi-component homogeneous mixed solvent:

15% ≤ ethylene carbonate ≤ 35%;
5% ≤ propylene carbonate ≤ 15%;
20% ≤ diethyl carbonate ≤ 40%;
10% ≤ ethyl propionate + propyl propionate ≤ 50%;
3% ≤ fluorobenzene ≤ 10%;

said additive combination comprises fluoroethylene carbonate, adiponitrile, and at least one compound having the structure shown in structural formula I:



Structural formula I

In structural formula I: A1 and A2 are hydrocarbylenes or oxygen partially substituted hydrocarbylenes, respectively, having 0–6 carbon atoms; R is a hydrogen atom, methyl, methylene, or cyano.

2. The wide-temperature-range homogeneous non-aqueous electrolyte solution of claim 1, characterized in that: the mass percentage content of said ethylene carbonate in the non-aqueous organic solvent is 20% to 25%.

3. The wide-temperature-range homogeneous non-aqueous electrolyte solution of claim 1, characterized in that: the mass percentage content of said fluoroethylene carbonate in the electrolyte solution is 0.5% to 7%.

4. The wide-temperature-range homogeneous non-aqueous electrolyte solution of claim 1, characterized in that: the mass percentage content of said adiponitrile in the electrolyte solution is 0.5% to 2%.

5. The wide-temperature-range homogeneous non-aqueous electrolyte solution of claim 1, characterized in that: the mass percentage content of the compound shown in structural formula I in the electrolyte solution is 0.5% to 5%.

6. The wide-temperature-range homogeneous non-aqueous electrolyte solution of claim 1, characterized in that: the compound shown in structural formula I is any one of succinonitrile, 2-methylglutaronitrile, 2-methyleneglutaronitrile, 1,4-dicyano-2-butene, 1,2-bis(2-cyanoethoxy)ethane, and 1,3,6-hexanetricarbonitrile.

7. The wide-temperature-range homogeneous non-aqueous electrolyte solution of claim 1, characterized in that: it also contains one or more additives of vinylene carbonate, vinyl

ethylene carbonate, 1,3-propane sultone, and vinyl sulfate, and the mass percentage of each of the described additives in the electrolyte solution is 0.1% to 5.0%.

8. The wide-temperature-range homogeneous non-aqueous electrolyte solution of claims 1–7, characterized in that: the components in said electrolyte solution are highly soluble with each other, and a homogeneous and stable state can be maintained even after storage for a long period of time in an environment below -30°C.

Wide-temperature-range homogeneous non-aqueous electrolyte solution

Technical Field

[0001] The present invention relates to the field of lithium-ion batteries, and specifically relates to a wide-temperature-range homogeneous non-aqueous electrolyte solution.

Background Art

[0002] Lithium-ion batteries have advantages such as high operating voltage, high specific capacity, long cycle life, no memory effect, and environmental friendliness, and are widely used in the digital, energy storage, power, and military aerospace fields. An electrolyte solution, as a carrier for ion transport in a lithium-ion battery, plays a critically important role in the performance of all aspects of the lithium-ion battery.

[0003] As consumer terminals demand ever-higher energy density from batteries, the development of high-energy density lithium-ion batteries has become an ongoing effort in this field. At the current stage, the energy density of lithium-ion batteries is improved primarily by selecting high-capacity, highly compact positive and negative electrode active materials and increasing the battery charge cut-off voltage.

[0004] However, increasing the charge cut-off voltage of a lithium-ion battery reduces the stability of the positive electrode material, accelerating the dissolution of transition metal ions in the positive electrode material and the oxidative decomposition of the electrolyte, degrading the performance of the battery.

[0005] Fluoroethylene carbonate (FEC) has good film-forming properties and resistance to oxidation, and when applied in a high-voltage lithium-ion battery electrolyte, can effectively improve its cycle performance. However, FEC is prone to decomposition at high temperatures, and the product hydrofluoric acid can exacerbate the dissolution of transition metal ions from the positive electrode material, easily causing the battery thickness to expand and the internal resistance to grow; lithium-ion batteries have poor high-temperature characteristics.

[0006] To address the problem of swelling of fluoroethylene carbonate at high temperatures, it is common in the industry to stabilize the positive electrode structure by means of adding organonitrile substances (CN 201110157665), thus improving, to a certain extent, the high-temperature performance of the battery. However, organonitriles are poorly soluble in electrolyte solution solvent systems, and the addition of them at higher ratios affects the lithium ion transport rate and the wettability of the electrolyte to the electrode material; there is also the problem of poor interfacial compatibility of the negative electrode and easy precipitation at low temperatures, severely limiting the cycling performance and low-temperature performance of a high-voltage battery.

[0007] In addition, ethylene carbonate (EC), a solvent commonly used in electrolytes, has a melting point of 35°C or higher, and conventional mixed solvent systems are prone to precipitate some EC at low temperatures and cannot form a homogeneous mixed-solution state.

[0008] In view of the foregoing, it is indeed necessary to provide an electrolyte solution that can remain homogeneous and stable over a wide temperature range in order to ensure that a lithium-ion battery has good high-voltage cycle performance and can perform at high and low temperatures.

Summary of the Invention

[0009] In view of the problems in the background art, the primary purpose of the present invention is to address the shortcomings of the prior art and to provide a wide-temperature-range homogeneous non-aqueous electrolyte solution that has good lithium ion transport properties, electrode plate wettability, and interfacial compatibility, while also resolving the problem of crystal precipitation at low temperatures.

[0010] In order to achieve the described purpose, the technical solution used in the present invention is:

[0011] a wide-temperature-range homogeneous non-aqueous electrolyte solution containing a non-aqueous organic solvent, electrolyte lithium salt, and additive combination; said non-aqueous organic solvent being the following multi-component homogeneous mixed solvent:

[0012] 15% ≤ ethylene carbonate (EC) ≤ 35%;

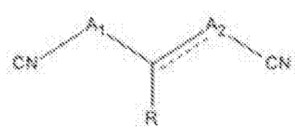
[0013] 5 % ≤ propylene carbonate (PC) ≤ 15%;

[0014] 20% ≤ diethyl carbonate (DEC) ≤ 40%;

[0015] 10% ≤ ethyl propionate (EP) + propyl propionate (PP) ≤ 50%;

[0016] 3% ≤ fluorobenzene (FB) ≤ 10%;

[0017] said additive combination comprises fluoroethylene carbonate (FEC), adiponitrile (ADN), and at least one compound having the structure shown in structural formula I:

[0018] 

Structural formula I

[0019] In structural formula I: A1 and A2 are hydrocarbylenes or oxygen partially substituted hydrocarbylenes, respectively, having 0–6 carbon atoms; R is a hydrogen atom, methyl, methylene, or cyano.

[0020] Preferably, the mass percentage content of said ethylene carbonate (EC) in the non-aqueous organic solvent is 20% to 25%.

[0021] Preferably, the mass percentage content of said fluoroethylene carbonate (FEC) in the electrolyte solution is 0.5% to 7%.

[0022] Preferably, the mass percentage content of said adiponitrile (ADN) in the electrolyte solution is 0.5% to 2%.

[0023] Preferably, the mass percentage content of the compound shown in structural formula I in the electrolyte solution is 0.5% to 5%.

[0024] Preferably, the compound shown in structural formula I is any one of succinonitrile, 2-methylglutaronitrile, 2-methyleneglutaronitrile, 1,4-dicyano-2-butene, 1,2-bis(2-cyanoethoxy)ethane, and 1,3,6-hexanetricarbonitrile.

[0025] Preferably, it also contains one or more additives of vinylene carbonate, vinyl ethylene carbonate, 1,3-propane sultone, and vinyl sulfate, and the mass percentage of each of the described additives in the electrolyte solution is 0.1% to 5.0%.

[0026] In the described technical solution, the components in said electrolyte solution are highly soluble with each other, and a homogeneous and stable state can be maintained even after storage for a long period of time in an environment below -30°C.

[0027] The advantages of the present invention are as follows.

[0028] 1. Fluoroethylene carbonate (FEC), which has good film-forming properties and resistance to oxidation; in the present invention, the addition of a reasonable amount ensures good high-voltage cycling performance of the battery without seriously affecting the high-temperature performance of the battery;

[0029] 2. Adiponitrile (ADN), which effectively complexes with the reactive metal ion reaction point in the positive electrode material, inhibiting the dissolution of the metal ions and the decomposition of the electrolyte solution, stabilizing the structure of the positive electrode material and improving the high-temperature performance of the battery to a certain extent; the addition of a smaller amount ensures uniform dissolution in the electrolyte, and is not prone to precipitation under low-temperature conditions.

[0030] 3. The compound shown in structural formula I also contains a cyano that can be complexed with transition metal ions, further improving the high-temperature performance of the battery. More specifically, in comparison with ADN, the compound shown in structural formula I has a polarity closer to that of the solvent and has better solubility in the electrolyte solution, without the problem of precipitation at low temperatures; at the same time, according to the principle of similar dissolution, the addition of the compound of structural formula I can lead to a molecular interaction with adiponitrile, facilitating the uniform dispersion of adiponitrile in the electrolyte solution and inhibiting the precipitation thereof at low temperatures.

[0031] 4. In the present invention, by means of reasonably controlling the content of the high-melting-point solvent component ethylene carbonate (EC) and adding propylene carbonate (PC) having a similar molecular weight and structure, the interaction between PC and EC facilitates the compatibility of EC with linear ester solvents and prevents the precipitation of EC crystals under low-temperature conditions.

[0032] 5. The introduction of new solvent components in the carbonate solvent system, with the aid of the property of low viscosity of carboxylic acid ester and the property of a lower contact angle of fluorobenzene, can effectively improve the wettability of the electrolyte solution to the electrode material and enhance the electrolyte lithium ion transport properties and negative electrode interfacial compatibility, compensating for the deficiencies of nitrile compounds in that regard.

[0033] The main innovations of the present invention are:

[0034] Excellent high-voltage cycling performance of the battery is ensured by means of the good film-formation performance of fluoroethylene carbonate (FEC), on the basis of which a nitrile compound is added to stabilize the structure of the positive electrode material, compensating for the high-temperature battery gas production problem caused by the FEC. Further, to prevent precipitation of crystals at low temperatures in high-voltage electrolytes, the principle of similar dissolution is used to introduce PC and the compound of structural formula I, which have structures similar to the components that readily precipitate at low temperatures (EC and ADN), respectively, effectively decreasing the freezing point of the mixed electrolyte solution, ensuring the homogeneous state of the electrolyte over a wide temperature range, improving the low-temperature performance of the high-voltage battery. Lastly, the carboxylic acid ester and fluorobenzene improve the electrolyte solution wettability performance on electrode materials and enhance the electrolyte lithium ion transport properties and negative electrode interfacial compatibility. The described optimized solution of an electrolyte solution ensures good high-voltage performance of a lithium-ion battery.

Brief Description of the Drawings

[0035] Figure 1 is a graph comparing the charging and discharging curves of 4.40 V graphite/$LiCoO_2$ polymer batteries, prepared from the lithium-ion battery electrolytes of Embodiment 1 and Comparison Example 1, after 500 cycles of 3.0–4.40 V at a 1C rate.

Detailed Description of the Preferred Embodiments

[0036] Embodiment 1

[0037] Electrolyte solution preparation steps: in a glove box filled with argon gas, ethylene carbonate, propylene carbonate, diethyl carbonate, fluorobenzene, ethyl propionate, and propyl propionate are mixed at a mass ratio of EC:PC:DEC:FB:EP:PP = 25:10:30:5:10:20; then, lithium hexafluorophosphate of a concentration of 1.0 mol/L is slowly added to the mixed solution, finally, the following are added on the basis of the total weight of the electrolyte solution: 4wt% of fluoroethylene carbonate (FEC), 2wt% of adiponitrile (ADN), 1wt% of succinonitrile (SN), 0.5wt% of 1,2-bis(2-cyanoethoxy)ethane (DENE), 0.2wt% of vinylene carbonate (VC), and 4.0wt% of 1,3-propane sultone; after stirring well, the lithium-ion battery electrolyte solution of Embodiment 1 is obtained.

[0038] Low-temperature storage of the electrolyte solution: the lithium-ion battery electrolyte solution prepared in the steps described above is loaded into a steel cylinder, which is pressurized with nitrogen as a protective gas; the cylinder is placed in a constant temperature and humidity chamber at -30°C; after 10 days of storage, the cylinder is opened to check for the precipitation of electrolyte crystals; if there is crystal precipitation, then the crystals are removed and are dissolved with DMC (dimethyl carbonate), and GC (gas chromatography) testing of the main components of the crystals is performed.

[0039] High-voltage battery electrical performance testing:

[0040] The lithium-ion battery electrolyte solution prepared in the steps described above is injected into a fully dried 4.40 V graphite/$LiCoO_2$ polymer battery; the battery is set aside at 45°C, and formed in a high-temperature fixture and sealed twice, then conventional classification of capacity is performed.

[0041] At 25°C, the capacity-classified battery is charged with constant current and voltage at 1C to 4.40 V, the cut-off current being 0.02C, and is then discharged at 1C constant current to 3.0 V. After 500 cycles of charging/discharging, the capacity retention rate at the 500th cycle is calculated. The calculation formula is as follows:

[0042] 500th cycle capacity retention rate (%) = (500th cycle discharge capacity / first cycle discharge capacity) × 100%

[0043] Embodiments 2–9 and Comparison Examples 1–6

[0044] In Embodiments 2–9 and Comparison Examples 1–6, Other than the electrolyte solution solvent and some additive composition and content added as shown in Table 1, all else is the same as in Embodiment 1. Table 1 lists the electrolyte solution partial component content, battery performance testing results, and low-temperature storage of Embodiments 1–9 and Comparison Examples 1–6:

[0045]

Embodiment	Solvent composition	FEC (%)	ADN (%)	Structural formula I additives (%)	Other additives (%)	Retention rate (%) after 500 cycles at 1C rate for 4.40 V at ambient temperature	Precipitation of crystals after storage for 10 days at -30°C
Embodiment 1	EC: PC: DEC: FB: EP: PP =25: 10: 30: 5: 10: 20	4	2	T_1: 1 T_2: 0.5	VC: 0.2 PS: 4	91.2	No precipitation
Embodiment 2	EC: PC: DEC: FB: EP: PP =25: 10: 30: 5: 10: 20	4	1	T_1: 2 T_2: 0.5	VC: 0.2 PS: 4	91.9	No precipitation
Embodiment 3	EC: PC: DEC: FB: EP: PP =25: 10: 30: 5: 10: 20	4	2	T_3: 1 T_2: 0.5	VC: 0.2 PS: 4	90.8	No precipitation

[0046]

Embodiment 4	EC：PC：DEC：FB：EP：PP =25：10：30：5：10：20	4	2	T_4：1 T_2：0.5	VC：0.2 PS：4	91.0	No precipitation
Embodiment 5	EC：PC：DEC：FB：EP：PP =25：10：30：5：10：20	5	2	T_2：2	VC：0.2 PS：4	92.2	No precipitation
Embodiment 6	EC：PC：DEC：FB：EP：PP =25：10：30：5：10：20	4	2	T_4：1 T_2：0.5	DTD：0.5 PS：3.5	91.6	No precipitation
Embodiment 7	EC：PC：DEC：FB：EP：PP =20：15：30：5：10：20	4	2	T_1：1 T_2：0.5	VC：0.2 PS：4	90.3	No precipitation
Embodiment 8	EC：PC：DEC：FB：EP：PP =20：10：35：5：10：20	4	2	T_1：1 T_2：0.5	VC：0.2 PS：4	91.5	No precipitation
Embodiment 9	EC：PC：DEC：FB：EP：PP =25：10：30：5：15：15	4	2	T_1：1 T_2：0.5	VC：0.2 PS：4	90.8	No precipitation
Comparison Example 1	EC：PC：DEC：FB：EP：PP =25：10：30：5：10：20	2.5	2	/	VC：0.2 PS：4	82.1	Small amount precipitated, main component ADN
Comparison Example 2	EC：PC：DEC：FB：EP：PP =25：10：30：5：10：20	4	2	/	VC：0.2 PS：4	84.3	Small amount precipitated, main component ADN
Comparison Example 3	EC：PC：DEC：FB：EP：PP =25：10：30：5：10：20	4	3.5	/	VC：0.2 PS：4	86.9	Large amount precipitated, main component ADN
Comparison Example 4	EC：DEC：FB：EP：PP=35：30：5：10：20	4	2	T_1：1 T_2：0.5	VC：0.2 PS：4	87.5	Precipitated, main components EC and ADN
Comparison Example 5	EC：PC：DEC=30：20：50	4	2	T_1：1 T_2：0.5	VC：0.2 PS：4	79.9	Precipitated, main components EC and ADN

[0047]

Comparison Example 6	EC：PC：DEC：FB＝30：15：50：5	4	2	T_1：1 T_2：0.5	VC：0.2 PS：4	81.1	Precipitated, main components EC and ADN

[0048] In Table 1 above, the abbreviated names of the chemical substances correspond as follows:

[0049] EC (ethylene carbonate); PC (propylene carbonate); DEC (diethyl carbonate); FB (fluorobenzene); EP (ethyl propionate); PP (propyl propionate); FEC (fluoroethylene carbonate); ADN (adiponitrile); T1 (succinonitrile); T2 (1,2-bis(2-cyanoethoxy)ethane); T3 (1,4-dicyano-2-butene); T4 (1,3,6-hexanetricarbonitrile); VC (vinylene carbonate); PS (1,3-propane sultone); DTD (ethylene sulfate).

[0050] From a comparison of Comparison Examples 1–3 in the table above with the embodiments, it can be known that the addition of FEC and ADN to the electrolyte solution improves the high-voltage cycling performance of the lithium-ion battery, and with the increase in added amounts of FEC and ADN, the capacity retention rate of the lithium-ion battery at 500 cycles of high voltage increases incrementally. However, the compound having the structure shown in structural formula I is not added to Comparison Examples 1–3, and the problem of ADN precipitation occurs in the electrolyte solution stored in a low-temperature environment for a long period of time; further, the higher the ADN content, the more crystals are precipitated; since Comparison Examples 1–3 lack the compound shown in structural formula I, their battery high-voltage cycling performances are also inferior to those of the embodiments.

[0051] The difference between Comparison Example 4 in the table above and the embodiments is that Comparison Example 4 does not use a PC solvent containing a structure similar to EC, and the problem of precipitation of EC occurs in the prepared electrolyte solution after long-term storage in a low-temperature environment. It is apparent that the PC in the electrolyte solution promotes the mutual solubility of EC components and linear ester solvents. At the same time, a homogeneous, stable electrolyte solution formed by the addition of a small amount of PC is conducive to improving the electrolyte lithium ion transport characteristics and the high-voltage cycling performance of the lithium-ion battery.

[0052] Comparison Examples 5 and 6 do not contain a low-melting-point carboxylic acid ester solvent, the mutual solubility of the components of the electrolyte solution is poor at low temperatures, precipitation of EC and ADN crystals also occurs, and a homogeneous electrolyte solution having a wide temperature range is not formed; the electrolyte solution lacks a carboxylic acid ester and fluorobenzene solvent that would improve the wettability of the electrode material and the electrode interfacial compatibility, and the high-voltage cycling performance of the lithium-ion battery is also far inferior to that of the embodiments.

[0053] In view of the foregoing, the present invention, by means of the addition of appropriate amounts of fluoroethylene carbonate (FEC) and adiponitrile (ADN), ensures good high-voltage cycling performance of a lithium-ion battery; at the same time, using the principle of similar dissolution, PC and the compound of structural formula I are introduced into the electrolyte solution, avoiding the problem of precipitation of crystals from the electrolyte solution at low temperatures; the carboxylic acid ester and fluorobenzene effectively improve the wettability of the electrolyte solution to the electrode material and enhance the electrolyte lithium ion transport properties and negative electrode interfacial compatibility, ensuring good high-voltage performance of the lithium-ion battery.

[0054] The above is a specific description of some embodiments of the present invention and is not intended to limit the patent scope of the present invention. Any variation or substitution that does not depart from the content of the present invention shall fall within the scope of protection of the present invention.

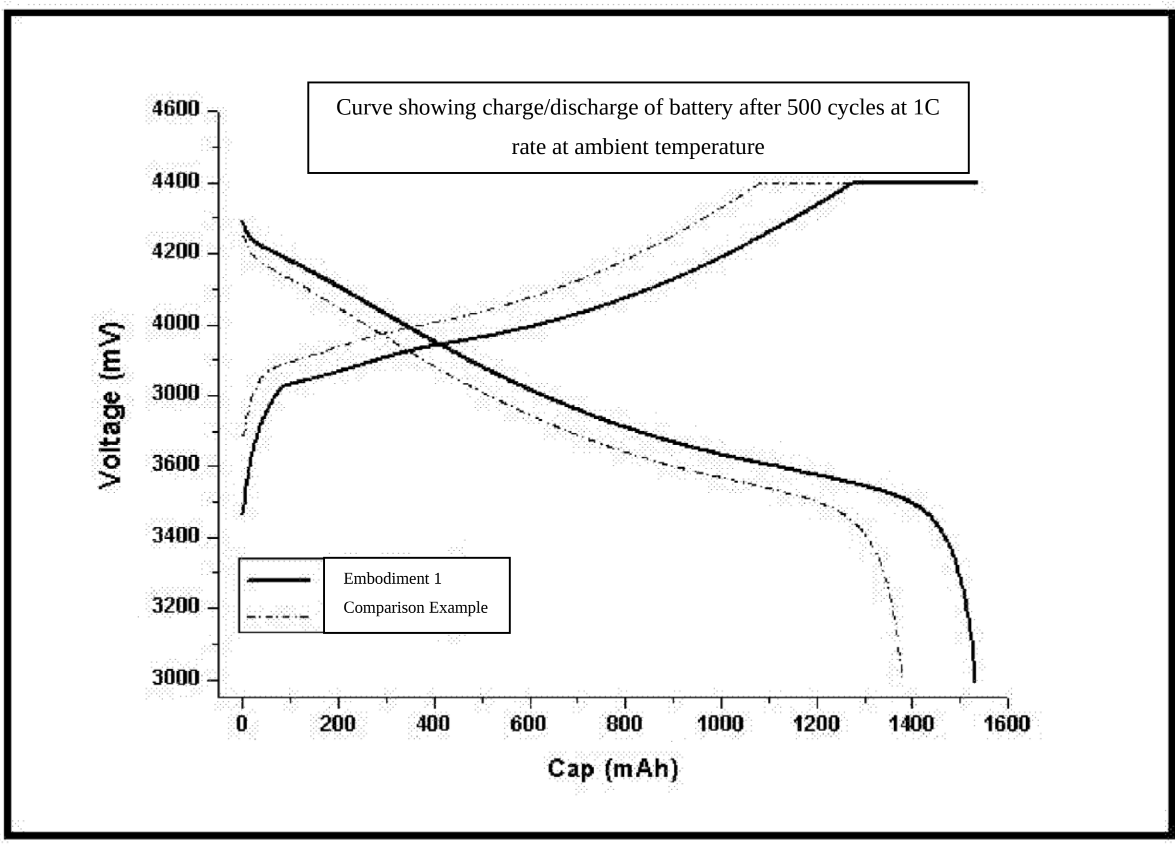

Curve showing charge/discharge of battery after 500 cycles at 1C rate at ambient temperature
Voltage (mV)
4600
4400
4200
4000
3000
3600
3400
3200
3000
Embodiment 1
Comparison Example
0
200
400
600
800
1000
1200
1400
1600
Cap (mAh)

FIG. 1

19 January 2023

CERTIFICATE OF ACCURACY

I, Aaron Hebenstreit, am competent to translate from Chinese into English and certify that the attached English language document(s) is a true and accurate translation of the original Chinese language document(s) CN106099187A to the best of my abilities.

I further declare that the statement in the preceding paragraph is true, and I understand that false statements and the like are punishable by fine and imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

Aaron Hebenstreit

ATA Certified Translator, Chinese > English

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