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Novel Phosphamide Additive to Improve Thermal Stability of Solid Electrolyte Interphase on Graphite Anode in Lithium-Ion Batteries

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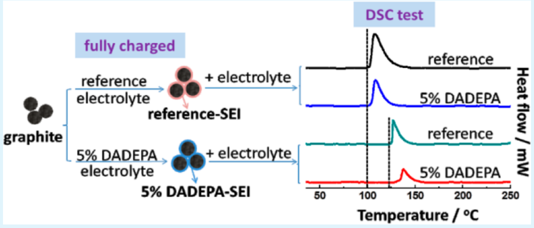
ABSTRACT: In this communication, a novel electrolyte additive, N,N-diallyic-diethyoxyl phosphamide (DADEPA), is described for the first time to improve the thermal stability of lithiated graphite anode in Li-ion batteries. The differential scanning calorimetry (DSC) measurement demonstrated that when the graphite was lithiated in the 5% DADEPA-containing electrolyte, the heat generation decreased sharply by half as compared with the reference, whereas the onset temperature for the main exothermic process was postponed by 20 °C. Electrochemical and XPS analyses indicated that the distinctive improvement in thermal safety came from a new interfacial chemistry, in which phosphorus-containing ingredients was embedded during the initial forming of the interphase.



KEYWORDS: *phosphamide, solid electrolyte interface (SEI), safety, lithium-ion batteries*

1. INTRODUCTION

Lithium-ion batteries constitute an important part of our daily life with their omnipresence in portable electronic devices, while their market is being further expanded into the applications in electrification of vehicles and large-scale stationary power grid storages in recent years.[1−3] However, the concern over the safety of this energetic chemistry remains the main obstruction to these latter efforts, which must be resolved before it can materialize in any large-format applications.[4]

One of the major contributions to battery safety hazard is the reactions between the organic electrolyte solvents and the charged electrodes. In particular, the parasitic reactions were accelerated at elevated temperatures, resulting in the catastrophic thermal runaway.[5] Among all the battery components participating these thermal reactions, the interphase formed between lithiated graphitic anode and electrolyte was identified to possess the lowest onset temperature, which would set off the chain-reaction once the generated heat could not be dissipated effectively.[5] Therefore, the thermal stability of the solid electrolyte interphase (SEI) on graphitic anode actually dictates the thermal stability of the entire Li ion cell.

One of the most effective and economical way to manipulate SEI properties is by adding certain active ingredients into the electrolyte at small concentrations, often known as additives. In this work, a novel additive, N,N-diallyic-diethyoxyl phosphamide (DADEPA) is designed and synthesized to serve the above purpose.

2. EXPERIMENTAL SECTION

DADEPA, i.e., $(C_2H_5O)_2P(O)\text{-}N(CH_2CH{=}CH_2)_2$ as the target product was synthesized by a facile method.[6] To a solution of diethyl phosphorochloridate (13.8 g, 80 mmol) in dry acetonitrile (100 mL) in an ice bath, a mixture of 8.7 g of N-2-propenyl-2-propen-1-amine (90 mmol) and 10.1 g of anhydrous triethylamine (100 mmol) was added slowly, and the reactant was stirred for 2 h at room temperature, followed by washing with 10% sodium bicarbonate solution, and then extracted with dichloromethane. The organic layer was dried with anhydrous sodium sulfate, concentrated under vacuum, and purified on silica gel column chromatography (petroleum ether-ethyl acetate, 1:1) to yield the desired product (17.9 g, 96% yield). ^1H NMR ($CDCl_3$, 400 MHz): δ 5.59−5.49 (m, 2H), 4.97 (d, J = 13.0 Hz, 4H), 3.91−3.75 (m, 4H), 3.41 (dd, J = 10.2 Hz, J = 6.6 Hz, 4H), 1.12 (t, J = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 134.0 (d, $J_{c\text{-}p}$ = 2.3 Hz), 117.3, 61.7 (d, $J_{c\text{-}p}$ = 5.5 Hz), 47.2 (d, $J_{c\text{-}p}$ = 4.3 Hz), 15.7 (d, $J_{c\text{-}p}$ = 7.2 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 9.48. ESI-MS: m/z = 234 $[M + H]^+$; 256 $[M + Na]^+$.

The electrolyte with DADEPA was obtained by directly adding the as-prepared DADEPA to the reference electrolyte (1.0 M $LiPF_6$ ethylene carbonate (EC)/ dimethyl carbonate (DMC) (1/1 by volume)) in concentration of 5% in volume. Corresponding electrochemical performances were tested in

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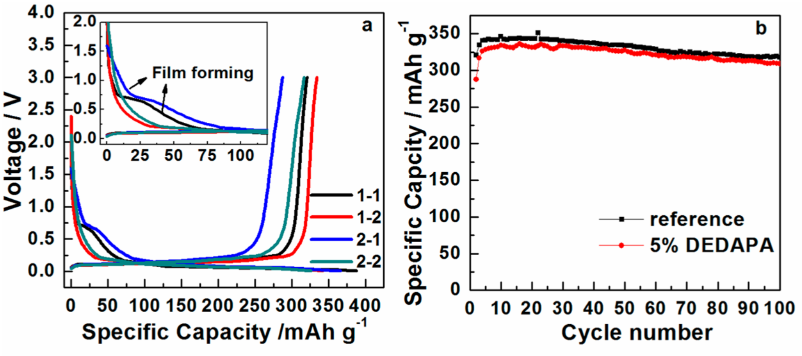

Figure 1. (a) Initial 2 charge/discharge cycles and (b) cycle performances of Li/graphite cells, curve 1−1, 1−2 are the first and second cycle of the cell without DADEPA, 2−1, 2−2 are that of the cell with DADEPA.

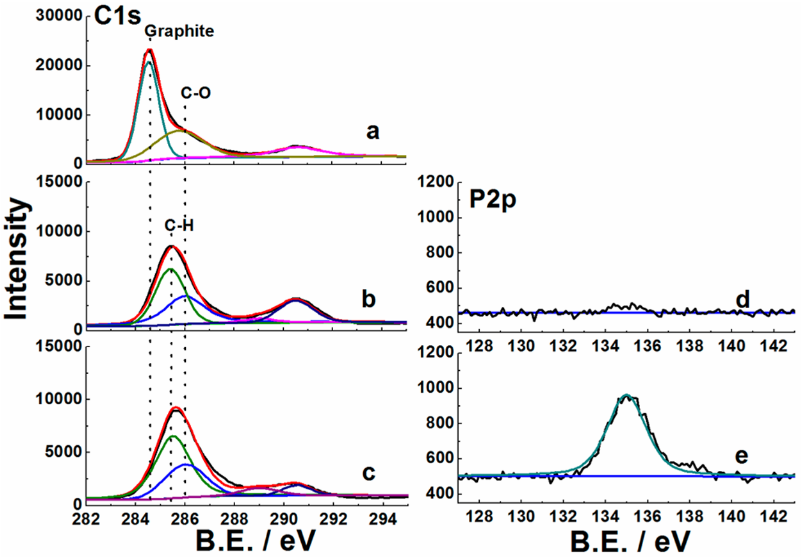

Figure 2. XPS spectra of (a) pristine electrode, and (b−e) electrodes after 2 cycles at a current density of 75 mA g^{-1} in the electrolytes (b, d) without and (c, e) with 5% DADEPA.

CR2025 coin-type cells (75 mA g^{-1}, 0.005−3.00 V, 30 °C) with graphite as working electrode against Li as counter electrode. The graphite electrode was mixed with modified natural graphite, acetylene black and poly(vinyldene fluode) (PVdF) at a weight ratio of 85:5:10. XPS (Quantum 2000, Physical Electronics) measurements were conducted to analyze the components of the surfaces of the pristine and cycled graphite electrodes. Before the XPS tests, cycled graphite electrodes were removed from cells (after 2 cycles) and washed with DMC. DSC (STA 409PC, Netzsch, Germany) tests of lithiated graphite powder in presence of electrolyte were carried out to analyze the thermal reactions between the two. Typically, 1 mg lithiated graphite powder ($Li_{0.9}C_6$) for DSC measurement was scraped off the fully charged electrode (in the second cycle) and washed with DMC, and then sealed in a high-pressure stainless steel pan together with 2 μL of testing electrolyte. The heat events were then recorded from room temperature to 250 °C at a heating rate of 10 °C min^{-1}.

3. RESULTS AND DISCUSSION

Figure 1a shows the charge/discharge profiles of Li/graphite cells during the initial two cycles in reference electrolyte and electrolyte with 5% DADEPA additive. Irreversible capacity loss exists in the first cycle in both cells, which is believed to be caused by electrolyte decomposition as part of the SEI formation process.[7] Upon closer examination, when 5% DADEPA is present, the formation process starts at 1.5 V, which is ca. 0.7 V higher than that of the reference electrolyte (~0.8 V), indicating that DADEPA may participate in the SEI formation on the graphite surface and decompose before the main electrolyte solvents do. The lower Coulombic efficiency (78.5%) in the presence of DADEPA as compared with that of reference (82.7%) may suggest that a thicker SEI has been formed. From the second cycle on, this irreversible process disappears for both cells. The cycling performances of these cells were shown in Figure 1b, where similar discharge capacity retentions were obtained with both the cells. It is known that phosphorus-based additives have certain negative effects on the graphite electrode. Compared with the typical phosphorus flame-retardant additives that have been reported,[8,9] and to the best of our knowledge, DADEPA shows the least electrochemical incompatibility with the graphite anode among those phosphorus additives reported.

To further confirm our assumption that DADEPA participates in the SEI forming process, XPS characterization experiments were carried out to analyze the surface species on the cycled graphite anode. Figure 2a−c show the C1s spectra collected from these electrodes. Compared with the pristine graphite surface, the most obvious difference detected after the electrodes were cycled in either reference or 5% DADEPA-containing electrolytes is that the main peak at 284.5 eV for elemental carbon is replaced by peaks of C−H (285.4 eV) and C−O (286.0 eV). This change reflects the coverage of the pristine graphite surface by typical decomposition products from the electrolyte solvents.[10,11]

While the peak at 290.5 eV corresponds to C−F for the binder PVdF in the pristine graphite electrode in Figure 2a,[10] it should be assigned to CO_3^{2-} and $RCH_2OCO_2^-$ group after cycling. The peak at about 289 eV should arise from semicarbonates $RCH_2OCO_2^-$.[10,11] In consideration of larger area of the peak at 290.5 eV when graphite electrode cycled in reference electrolyte (Figure 2b) and larger area of the peak at 289 eV when cycled in the 5% DADEPA-containing electrolyte (Figure 2c), we speculate that SEI might be dominated by Li_2CO_3 when it was formed in the reference electrolyte, while more semicarbonate RCH_2OCO_2Li is formed as SEI ingredient when DADEPA is in the electrolyte. Moreover, significant distinction can also be found in P2p spectra as show in panels d and e in Figure 2. An obvious peak (135 eV), which can be assigned to P═O group in phosphate species,[12] shows on the electrode cycled in 5% DADEPA-containing electrolyte. As this peak intensity is negligible for the electrode cycled in the reference electrolyte, we can conclude with confidence that DADEPA should be its source, whereas $LiPF_6$ should be excluded. In other words, it provided the most direct evidence that DADEPA participates in the SEI forming process and introduces phosphorus component into the composition of the SEI film.

DSC tests were then conducted to investigate the effect of DADEPA additive on thermal stability of the graphite electrodes lithiated in either reference electrolyte or DADEPA-containing electrolyte. To make the studies thorough and systematic, four possible scenarios were considered, where these graphite electrodes were lithiated either in reference electrolyte (hence the SEI originated from reference, hereafter designated as ref-$Li_{0.9}C_6$) or in electrolytes containing 5% DADEPA (hence protected by DADEPA-originated SEI, hereafter designated as DADEPA-$Li_{0.9}C_6$), and additional electrolytes with or without DADEPA additive were mixed with these graphite anodes for DSC evaluation. Figure 3a−d showed the spectrum of thermal stabilities of these four combinations. As shown in Figure 3a−d, exothermic peak at around 100−170 °C is often identified as the onset decomposition of the metastable SEI (formed during the charge/discharge cycle) and reformation of a more stable layer on graphite surface.[13] More specially, the exothermic peak, which starts at around 100 °C in panels a and b in Figure 3 for ref-$Li_{0.9}C_6$with reference and DADEPA-containing electrolytes shifts to higher temperatures of 125 °C in Figure 3c and 130 °C in Figure 3d when the graphite is changed to DADEPA-$Li_{0.9}C_6$.

Besides onset temperatures, the amount of heat generation in this process is also significantly affected by additive, as exemplified by the combination of DADEPA-containing electrolyte and DADEPA-$Li_{0.9}C_6$ (297 mJ) and the other extreme of the combination of reference electrolyte with ref-$Li_{0.9}C_6$ (987 mJ). Between these two extremes are the other two combinations with medium amount of heat generation, i.e., 412 mJ for DADEPA-$Li_{0.9}C_6$ with reference electrolyte and 599 mJ for ref-$Li_{0.9}C_6$ with DADEPA-containing electrolyte.

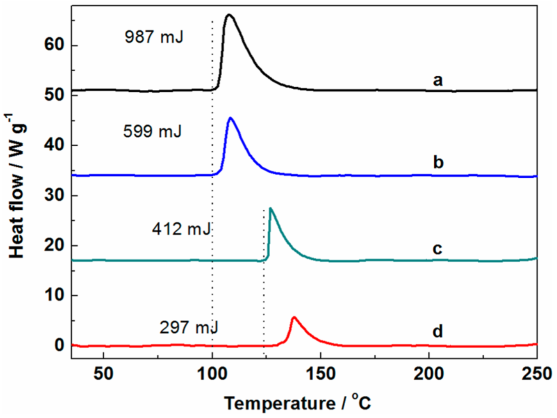

Figure 3. DSC curves of 1 mg $Li_{0.9}C_6$ powder (lithiated in reference electrolyte) + 2 μL electrolytes (a) without and (b) with 5% DADEPA; and 1 mg of $Li_{0.9}C_6$ powder (lithiated in 5% DADEPA-containing electrolyte) + 2 μL of electrolytes (c) without and (d) with 5% DADEPA.

These results clearly suggest that the thermal stability of the SEI layer formed in the electrolyte with 5% DADEPA is improved as compared to that formed in the reference electrolyte. According to the XPS results discussed before, it is believed that P-containing species in the SEI film is a main contributor to the improvement of the thermal stability. It is well-known that phosphorus is an important component for flame-retarding materials, with the possible flame-retarding mechanism being the generation and propagation of radicals that inhibits the oxidation process.[14] We believe similar mechanism could be responsible here in our thermally stable SEI system, since SEI is a surface layer of complicated morphology consisting of both small ionic species (salt) and macromolecules. Polymeric carbon-based compounds could have been formed during the charge/discharge process.[15]

Furthermore, for a given $Li_{0.9}C_6$ powder, the detected heat generation is smaller when the additional electrolyte has DADEPA. These data indicate that DADEPA in the bulk electrolyte can also mitigate the heat generation regardless where SEI has been formed. So the system of DADEPA-$Li_{0.9}C_6$ mixed with 5% DADEPA-containing electrolyte, which combines both the safer SEI layer and safer electrolyte, presents the least thermally activity.

4. CONCLUSION

A novel electrolyte additive DADEPA is designed and synthesized in this work. The presence of 5% DADEPA in reference electrolyte significantly mitigates the thermal reactivities between the lithiated graphite and the electrolyte, although its electrochemical compatibility with graphite electrode remains to be improved. The thermal stability of lithiated graphite protected by DADEPA-originated SEI is remarkably improved compared to that of the graphite protected by SEI formed in reference electrolyte, as demonstrated both in terms of onset temperatures and heat generation. Besides, the thermal stability of the bulk electrolyte is also improved with the addition of DADEPA. This exploration of electrolyte additives for better thermal stability of Li-ion batteries will benefit the adoption of this battery chemistry into large scale applications.

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Notes

The authors declare no competing financial interest.

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