Short communication

Aromatic isocyanate as a new type of electrolyte additive for the improved performance of Li-ion batteries

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Abstract

Aromatic isocyanate, 4-fluorophenyl isocyanate and phenyl isocyanate, were first used to reduce the initial irreversible capacities during the formation of the solid electrolyte interface (SEI) on a graphite surface. Results showed that the addition of 1–5 wt.% isocyanate to propylene carbonate-containing electrolytes could effectively reduce the initial irreversible capacities in the SEI formation and increase the cycleability of Li-ion batteries. The improvement is attributed to the high reactivity of isocyanate with chemisorbed oxygen groups, such as carboxyl and phenol, which are inevitably present in the prismatic (edge) sites of graphite and are known among the sources to cause the initial irreversible capacities of a graphite anode. It is proposed that the isocyanate reacts with carboxyl and phenol groups to form more stable products, and that the resulting products have a better affinity to the subsequently formed SEI. In addition, the presence of isocyanate assists in scavenging water and acidic HF impurities from the electrolyte.
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Keywords: Isocyanate; Electrolyte additive; Graphite; Solid electrolyte interface; Li-ion battery

1. Introduction

Graphite has been the most widely used anode material in Li-ion batteries due to its high capacity and low potential. Reversible intercalation reactions of Li^{+} ions with graphite are attributed to the formation of a stable and protective solid electrolyte interface (SEI) on the graphite surface, which is generally completed during the initial few cycles [1,2]. Previous studies have shown that the SEI formation and its related irreversible capacity are largely affected by the morphology and surface chemistry of graphite [3–5]. In view of the architectural structure, graphite particles contain two types of surfaces: basal plane surfaces and prismatic (edge) surfaces. The ideal basal plane surfaces (free of defects and contaminants) are homogeneous and consist only of carbon atoms, while the prismatic surfaces are heterogeneous and apart from carbon atoms contain numerous chemical complexes that are formed during the manufacturing steps [6–9]. These complexes mostly are carbon–hydrogen bonds [6,7] and chemisorbed oxygen groups, such as carboxyl,
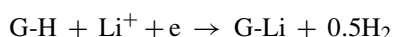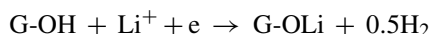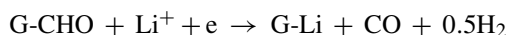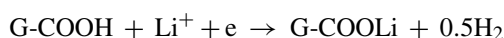
carbonyl, lactone and phenol [8,9]. Theoretically, the intercalation reactions of Li^{+} ions take place on the prismatic surfaces, and there are no Li^{+} ion transportations occurring on the basal planes. Therefore, morphology and chemistry of the prismatic surfaces play a major role in affecting the initial irreversible capacities of the graphite anode [5]. According to the type of reactions, the irreversible capacities are categorized as two major sources: (1) solvent reduction as a result of the co-intercalation of solvent molecules into graphite, and (2) reduction of the chemical complexes on the prismatic surfaces of graphite. The former is more associated with the surface morphology, and the latter with surface chemistry. To modify the surface morphology, the graphite materials were physically coated with a protective layer, such as a metal oxide [10–12], H_3BO_3–$H_2C_2O_4$ anhydride [13], alkali metal carbonate [14,15], metal [16,17], disordered carbon [18,19] and polymer [20,21]. It is believed that the coating layers preferably cover the prismatic areas, which in turn suppress the solvent co-intercalation with the solvated Li^{+} ions. Alternatively, many reductive compounds, such as vinylene carbonate [22], vinyl ethylene carbonate [23], vinyl acetate [24], acrylic acid nitrile [25], ethylene sulfite [26], propylene sulfite [27], SO_2 [28], CS_2 [29] and so forth have been used as the electrolyte additive to facilitate the SEI formation. Basically,

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these additive molecules are electrochemically reduced at higher potentials than the solvent reduction, and the resulting insoluble products are subsequently coated onto the prismatic sites of graphite as the preliminary SEI film (or called as the SEI nuclei for the following growth), which hence suppresses the solvent co-intercalation.

The portion of the initial irreversible capacities by graphite is attributed to a series of electrochemically induced reductions of the chemical complexes on the prismatic surfaces, for example (where "G-" represents graphite):

$$G\text{-COOH} + Li^+ + e \rightarrow G\text{-COOLi} + 0.5H_2$$

$$G\text{-CHO} + Li^+ + e \rightarrow G\text{-Li} + CO + 0.5H_2$$

$$G\text{-OH} + Li^+ + e \rightarrow G\text{-OLi} + 0.5H_2$$

$$G\text{-H} + Li^+ + e \rightarrow G\text{-Li} + 0.5H_2$$

Since the concentration of the chemical complexes in the prismatic surfaces is low, these reductions usually take place at lower potentials than the solvent reduction, or mostly are in parallel with the interaction of Li^+ ions into graphite. To minimize these irreversible capacities, chemical modifications have been adopted to deactivate or remove these chemical complexes from the prismatic surfaces. The successful examples include silylation [9], mild oxidization [6,7,30] and reactive induction thermal plasma [31], all of which however seem rather complicated and time inefficient. To simplify the process of chemical modifications, this laboratory first proposed isocyanate as the electrolyte additive to modify in situ the prismatic surfaces of graphite [32]. Based on this idea, in the present work the impact of two aromatic isocyanates, 4-fluorophenyl isocyanate and phenyl isocyanate, on the initial irreversible capacity and cycleability of graphite will be presented, and the mechanism of these additives to facilitate the SEI formation will be proposed.

2. Experimental

Salt $LiPF_6$ (Stella Chemifa Corp.), 4-fluorophenyl isocyanate (FPIC, 99%, Aldrich), and phenyl isocyanate (PIC, >98%, Aldrich) were used as received. Propylene carbonate (PC), ethylene carbonate (EC) and ethyl methyl carbonate (EMC, all from Ferro Chemical) were dried over neutral alumina until their water levels dropped to below 20 ppm. Using the materials above, a series of electrolytes with and without the additive were prepared in an argon-filled glove-box. To describe the composition of the electrolytes, the weight ratio and weight percentage are used for the solvent and additive, respectively. Electrode films of the graphite anode and lithium nickel-based mixed oxide cathode, kindly provided by Saft America, were punched into small discs with an area of $1.27\,cm^2$ and dried at $110\,^{\circ}C$ under vacuum for 16 h. Using Celgard® 2500 membrane as the separator, BR2335-size button cells of Li/graphite and graphite/cathode were assembled and filled with 80 μl of the given electrolyte in the same glove-box. In Li/graphite half-cell, a small piece of Li foil was used as the reference electrode by sandwiching it between the graphite and Li counter electrode.
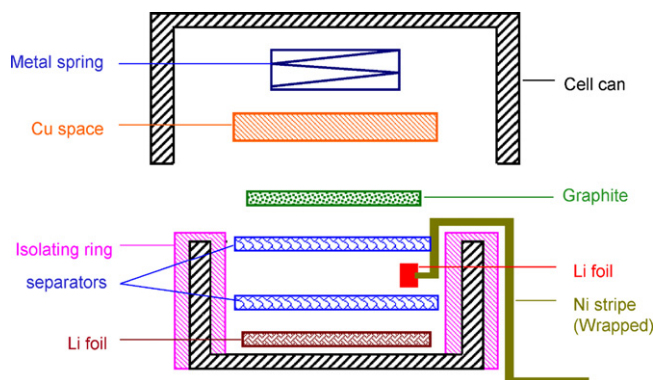

Fig. 1. A scheme of 3-electrode Li/graphite button cells.

To do this, the Li foil was pressed onto one end of a strip of thin Ni foil and carefully wrapped with the separator to isolate from the electrodes and the button cell frame. A scheme of the 3-electrode button cell is illustrated in Fig. 1.

A Solartron SI 1287 Electrochemical Interface and SI 1260 Impedance/Gain-Phase Analyzer were employed to perform cyclic voltammetric tests and measure cell impedances. The cells were cycled on a Maccor Series 4000 tester between 0.002 and 1.0 V for Li/graphite half-cells and between 2.5 and 3.9 V for Li-ion full cells, respectively. For Li-ion full cells, all the charging processes were at a current limit of $0.1\,mA\,cm^{-2}$ after the cell voltage reached 3.9 V and remained at 3.9 V for an extended tickle charge.

3. Results and discussion

Fig. 2 shows the effect of aromatic isocyanate additives, FPIC and PIC, on the SEI formation of graphite in different electrolytes. It is shown in Fig. 2a that graphite was able to form a SEI in a 1.0 m $LiPF_6$ 1:1:3 PC/EC/EMC electrolyte without or with the presence of FPIC. There was a small cathodic current peak at 0.8–0.9 V versus Li^+/Li in both electrolytes, which are known to be the reduction of carbonate solvents, and is attributed to successful SEI formation. A calculation indicates that the cycling efficiencies of graphite in these two electrolytes were very close to each other although the peak current in the presence of FPIC was a little higher, as shown in the inset of Fig. 2a. This fact suggests that FPIC neither reduces irreversible capacities nor suppresses solvent reduction. When the content of PC was increased to 30%, the SEI formation failed in the control electrolyte due to the unsuppressed reduction of PC solvent at 0.6–0.7 V versus Li^+/Li, whereas it succeeded with the addition of 5% FPIC (Fig. 2b) showing a small cathodic current peak near 0.81 V versus Li^+/Li as the indication of SEI formation. Since the reduction peak potentials for the SEI formation in Fig. 2a and Fig. 2b were almost the same and their values reflected the suppressed reduction of carbonate solvents, a new mechanism might be proposed to explain the role of FPIC in facilitating the SEI formation of graphite in a PC-containing electrolyte.

As described in the introduction, there are numerous chemisorbed oxygen groups on the prismatic surfaces of graphite. Some of these groups, such as carboxyl and phenol, can
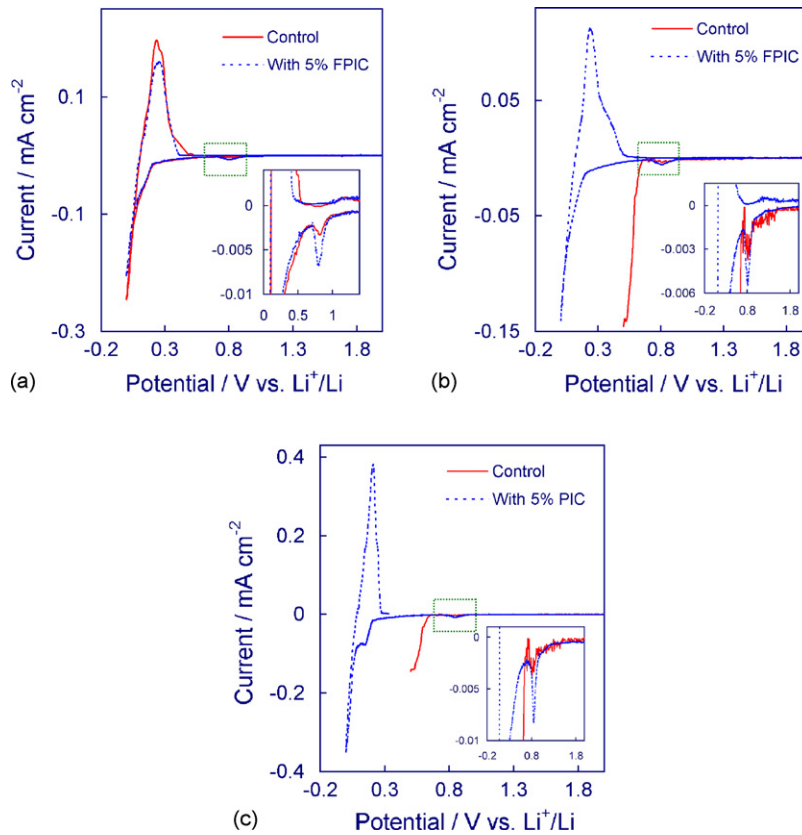
Fig. 2. Cyclic voltammogram of the first cycle of Li/graphite cell in different electrolytes without and with 5% of FPIC (a and b) or PIC (c) as the electrolyte additive. (a) 1.0 m LiPF$_6$ 1:1:3 PC/EC/EMC, (b) 1.0 m LiPF$_6$ 3:3:4 PC/EC/EMC and (c) 1.0 m LiPF$_6$ 3:3:4 PC/EC/EMC. Potential scanning rate was 0.01 V s^{-1}.

be reacted by isocyanate molecules to form more stable products, for example:

where "G" represents "Graphite"
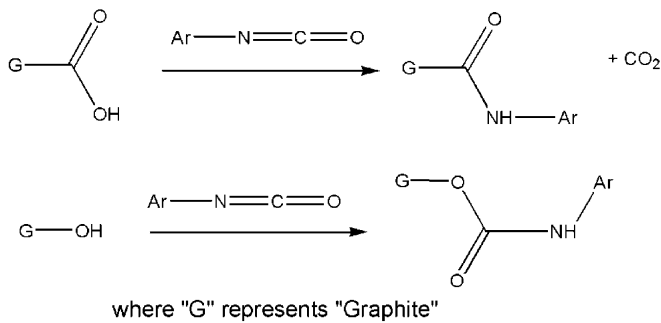
The resulting products (amide and carbamate) have better affinity for the decomposed products of carbonate solvents, which promotes the nucleation and the subsequent growth of the SEI, and it consequently suppresses further reduction of the solvents. According to this mechanism, the isocyanate itself does not involve any reductions, and its presence should not change the potential of the cathodic current peak for the SEI formation. This speculation is in good agreement with the results of Fig. 2a and Fig. 2b. On the other hand, the proposed mechanism indicates that substituent in the aromatic ring does not participate into any reactions, which means that changing the type of substituents should not affect the potential of the SEI formation. To

confirm this, PIC that contains no fluoride atoms was used to replace FPIC and the same experiment was performed as shown in Fig. 2c. Comparing the insets of Fig. 2b and Fig. 2c, one finds that both PIC and FPIC resulted in the same potentials for the SEI formation. This observation is in accordance with what the proposed mechanism predicts.

A galvanostatic cycling test was designed to confirm the results of cyclic voltammetry. Fig. 3 compares potential curves of the first cycle of Li/graphite cells using the electrolytes without and with FPIC, respectively. It is measured from Fig. 3a that in a 1:1:3 PC/EC/EMC solvent, two cells without and with FPIC generated the same irreversible capacities (9%). More interestingly, the potential of two cells in the initial period was completely overlapped (see the inset of Fig. 3a). This observation exactly reproduced the result of Fig. 2a, and it further verified the conclusion that the presence of FPIC did not change the potential for the SEI formation. In a 1:1 PC/EC solvent (Fig. 3b), the potential of the control cell indefinitely stayed at 0.7–0.8 V versus Li$^+$/Li, showing that no SEI could be formed and PC reduction was remained until the experiment ended. On contrary, the cell with the addition of 5% FPIC could be cycled reversibly with an initial cycling efficiency of over 90% although there was no characteristic reduction plateau of the FPIC reduction. The other important feature of the isocyanate additive in Li-ion batteries is its ability to scavenge water and acidic HF impurities from the electrolyte through the reactions below:
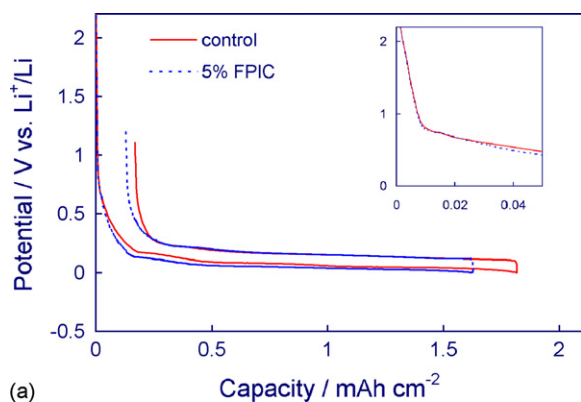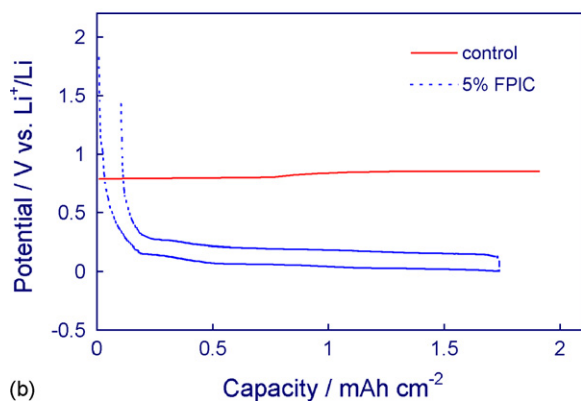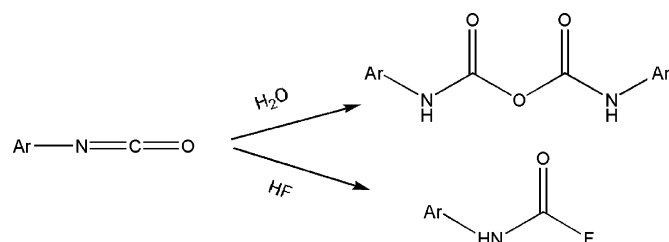
Fig. 3. Potential curve of the first cycle of Li/graphite cell in different electrolyte without and with 5% of FPIC, which was recorded at a current density of $0.1\,\text{mA cm}^{-2}$. (a) $1.0\,\text{m}$ LiPF$_6$ 1:1:3 PC/EC/EMC and (b) $1.0\,\text{m}$ LiPF$_6$ 1:1 PC/EC.

It has been known that the presence of water accelerates the hydrolysis of LiPF$_6$ to release acidic POF$_3$ and HF, and the resulting acids will further decompose the alkali SEI components. Furthermore, HF has been identified as the major source for the dissolution of cathode materials, being responsible for the capacity fading of Li-ion batteries. Therefore, the isocyanate additive is of special interest in the research and development for the improved performance of Li-ion batteries.

An overall comparison for the impact of FPIC and PIC on the cycling performance of Li-ion cells is presented in Fig. 4. It is obvious that that the capacities of cells with the additive, either FPIC or PIC, were gradually increased during the initial 10 cycles, while that of the control cell exhibited a slow and smooth fading. This phenomenon could be associated with the gradually increased wettability of graphite as a result of the slow reactions between isocyanate and chemisorbed oxygen groups on the prismatic surfaces. More importantly, the capacity of the control cell
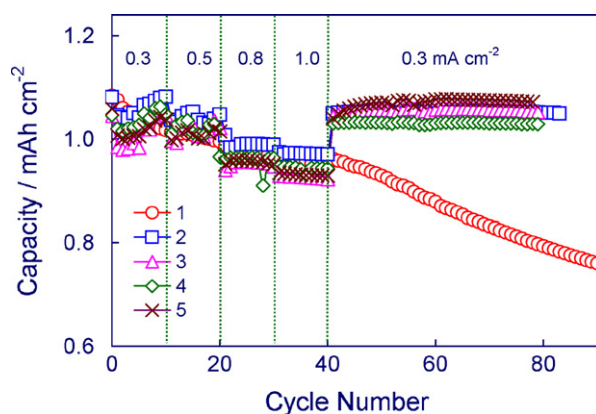

Fig. 4. Comparison of the impact of FPIC and PIC on the cycling performance of Li-ion cell in (a) $1.0\,\text{m}$ LiPF$_6$ 1:1:3 PC/EC/EMC and (b) $1.0\,\text{m}$ LiPF$_6$ 3:3:4 PC/EC/EMC, respectively, at a discharge current density of $0.5\,\text{mA cm}^{-2}$. (1) Electrolyte (a), (2) (a) + 5% FPIC, (3) (a) + 5% PIC, (4) (b) + 5% FPIC and (5) (b) + 5% PIC.

declined rapidly with the progressive cycling, while those of the cells containing additive remained very stable. Furthermore, there was very little difference in the capacity retention between FPIC and PIC. The facts above verify that the improvement by isocyanate has nothing to do with the substituent, fluoride, in the aromatic ring.

Fig. 5 displays the correlation of capacity retention and isocyanate concentration for the Li-ion cells using $1.0\,\text{m}$ LiPF$_6$ 3:3:4 PC/EC/EMC electrolyte. As described in Fig. 2b and Fig. 2c, the control cell could not be cycled due to its inability to form a stable SEI (not shown in Fig. 5). Even with the addition of as low as 1% PIC into the electrolyte, however, the cell could be cycled very well. It appears that further increase in the concentration of PIC did not improve the capacity retention significantly. This may be attributed to the low concentration of chemisorbed oxygen groups on the prismatic surfaces of graphite so that 1% PIC would be sufficient to react with these groups. Starting about the 120th cycle, all the cells suffered an accelerated capacity fading with unknown reasons. Therefore, further works are needed to understand this new type of additives.

To determine the optimized concentration of the isocyanate additive, the voltage curves of the Li-ion full cells containing
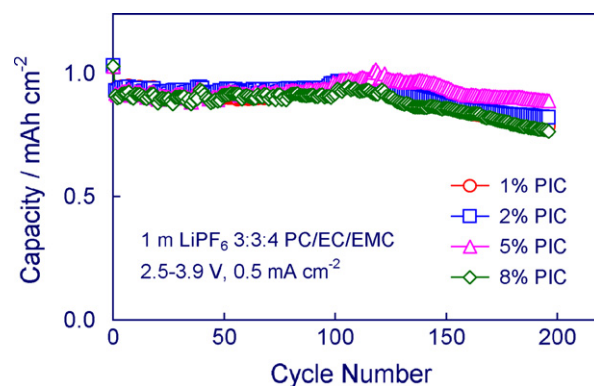

Fig. 5. Effect of the additive concentration on the cycling performance of Li-ion cell in $1.0\,\text{m}$ LiPF$_6$ 3:3:4 PC/EC/EMC at a discharge current density of $0.5\,\text{mA cm}^{-2}$.
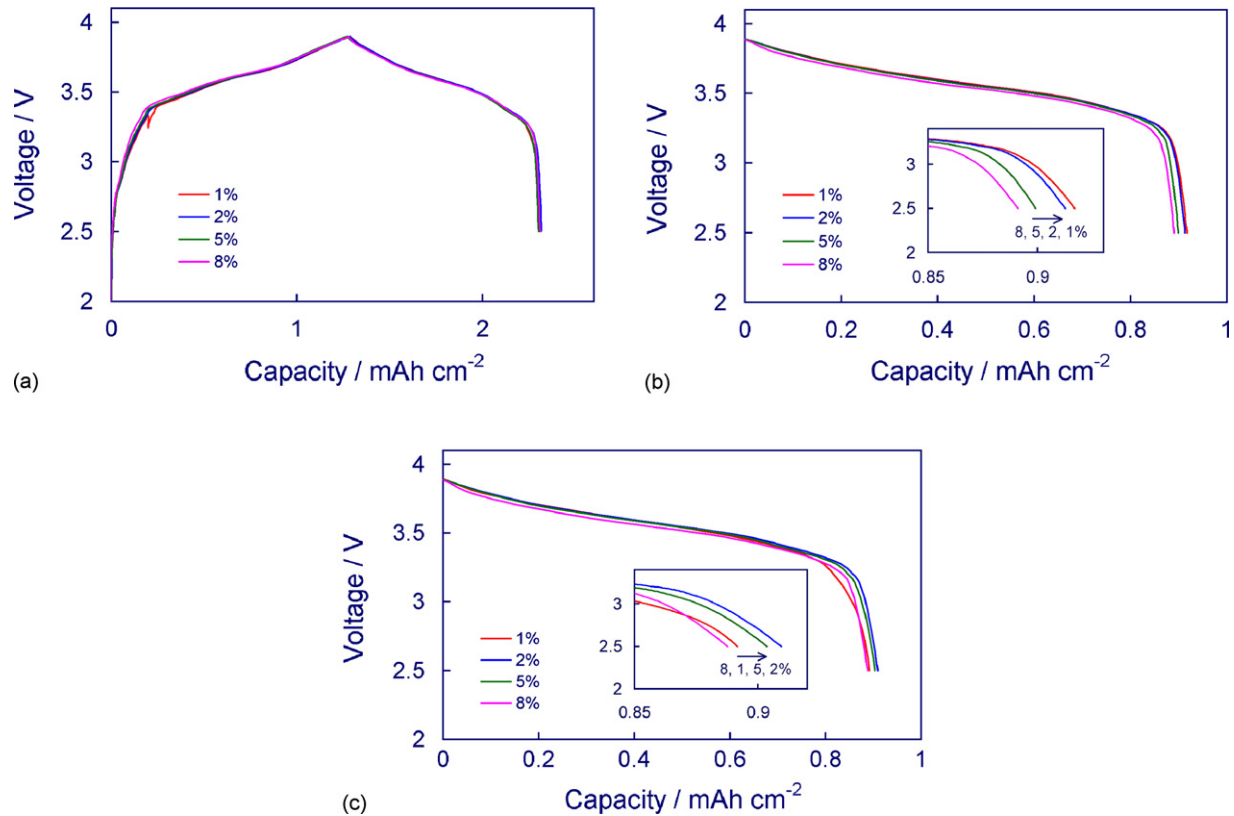
Fig. 6. Comparison of the voltage curves of Li-ion cells in 1.0 m LiPF$_6$ 3:3:4 PC/EC/EMC electrolyte containing different concentrations of PIC. (a) First forming cycle at 0.1 mA cm^{-2}, (b) 5th cycle at 0.5 mA cm^{-2} and (c) 80th cycle at 0.5 mA cm^{-2}.

different amount of PIC additive are compared in Fig. 6. In the first cycle during which the SEI was assumed to be completed (Fig. 6a), there were no differences in both the charging voltage profiles and cycling efficiencies (80.5%) among these cells containing 1, 2, 5 and 8%, respectively, of PIC. However, the excess isocyanate introduced a slightly negative impact for the extended cycles, as shown in the inset of Fig. 6b for the 5th cycle and Fig. 6c for the 80th cycle, respectively. According to the inset of Fig. 6c, the optimized concentration of PIC would be in a range of 2–5%.

After 200 cycles, all the cells were charged to the same state-of-charge (3.8 V), followed by an impedance measurement. The recorded impedance spectra showed the regular patterns as observed previously from the other Li-ion button cells [33,34], which could be well fitted using three resistance elements: buck resistance (R_b), SEI resistance (R_{sei}) and charge-transfer resistance (R_{ct}). The values of these three resistances fitted from the cell impedance spectra using ZView® software are summarized in Table 1, which shows that the reasonable concentration of PIC would be in a range of 1–5%. When the concentration of PIC was lower than 1%, the number of isocyanate groups could not be enough to convert the surface oxygen groups of graphite into more stable products so that the preliminary SEI could not be formed effectively. On contrary, when the concentration of PIC exceeded 5%, some negative impacts were introduced, which consequently resulted in the high cell impedance as indicated in the case of 8% PIC in Table 1.

Table 1
Summary of the element resistances of Li-ion cells

PIC concentration (%)	R_b (Ω)	R_{sei} (Ω)	R_{ct} (Ω)
1	2.7	9.4	18.8
2	2.8	7.3	18.1
5	2.96	10.3	25.3
8	5.5	20.9	24.9

Note: The data was fitted from the impedance spectra of Li-ion cells using 1.0 m LiPF$_6$ 3:3:4 PC/EC/EMC electrolyte with different concentrations of PIC, which were measured at 3.8 V after the cells were charged and discharged for 200 cycles.

4. Conclusions

In conclusion, aromatic isocyanates were effective in reducing the initial irreversible capacities and facilitating SEI formation on graphite in a PC-containing electrolyte. The mechanism for the isocyanates to promote the SEI formation is different from the conventional reductive additives, such as vinylene carbonate and vinyl ethylene carbonate, which are known to be electrochemically reduced at higher potentials than the electrolyte solvents. A possible mechanism for the isocyanate additives is that they react with the chemisorbed oxygen groups on the prismatic (edge) surfaces of graphite to form more stable products, and the resulting products have a better affinity for the subsequently formed SEI components. As a result, the reduced products of the solvent molecules can be effectively accumulated on the

graphite surface to establish the nucleation and the subsequent growth of the SEI, which therefore suppresses further reduction of the solvent molecules. Since only the isocyanate group is involved in the reactions, the type of substituents in the aromatic ring has no distinct impact on the improving effectiveness of the aromatic isocyanate additives. In addition to facilitating the SEI formation, the isocyanate additives are able to scavenge water and acidic HF impurities from the electrolyte. Therefore, the isocyanate compounds would be a new type of multifunctional additive for the improved performance of Li-ion batteries.

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