Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Journal of
Materials Chemistry A

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Hexamethylene Diisocyanate as an Electrolyte Additive for High-energy density Lithium Ion Batteries

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Hexamethylene diisocyanate can chemically react with the onium ion produced by the oxidation of propylene carbonate and *in-situ* generate a novel interfacial layer stabilized at high potential. With appropriate thickness of this film, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ presents the significantly improved rate and cycle performances when tested between 2.5 ~ 4.6 V(*vs.* Li/Li$^+$).

Lithium ion battery (LIB) has been rapidly developed since the first commercialization released in 1990s by Sony[1]. Till to date, this technology has dominated the market of commercial electronic devices and penetrated into the fields of transportations and smart grids [2]. In contrast to aqueous system[3], LIB electrolytes utilized liquid carbonates as solvents, which enabled the operating window widened to 1.2 ~ 4.3 V(*vs.* Li/Li$^+$)[4]. Although the anodic working potential was pushed to ~ 0.02 V(*vs.* Li/Li$^+$) by the efforts on solid electrolyte interphase (SEI) layer[5], the progress to lift cathode limitation almost kept static for most of solid remnants started to decompose above 4.35 V(*vs.* Li/Li$^+$)[4]. In the other hand, to positively widen working window could provide the possibility to fully utilize the commercial cathodes such as $LiCoO_2$ and $LiNi_{1-x-y}Co_xMn_yO_2$, and enable the evaluation of novel materials including $xLi_2MnO_3 \cdot (1-x)LiMnO_2$ and $LiNi_{0.5}Mn_{1.5}O_4$[6]. Obviously, high-potential electrolyte has become one of the most promising strategies to enhance the cell's energy density.

The utilization of anti-oxidative solvents seems to be the most easily implemented solution. The solvents with strong electron-withdrawing groups, such as sulfone and nitrile[7], could endure the oxidation at high potential. Although they exhibited good stability even up to 6 V(*vs.* Li/Li$^+$), the electrolytes based on these solvents are not applicable in current commercial system due to the inability to construct the effective SEI layer on graphite anode[8]. Currently, these solvents are utilized as co-solvents, by which the cut-off potential could be lifted for 100 ~ 200 mV. This

improvement could be attributed to the absorption of the anti-oxidative solvents on the active sites of cathodes [7b, 9].

To passivize the cathode with an inert layer is an alternative strategy to improve its cyclic stability. Coating inorganic ceramics, such as metal oxides and phosphates, could alleviate the side reactions between the electrolyte solvents and cathodes to enable $LiCoO_2$ working normally at 4.4 V(*vs.* Li/Li$^+$) with the state-art-of electrolyte[10]. Building an organic film with lower HOMO levels is also a do-able strategy, such as the fluorinated decomposed products of phosphides. The fluorine-contained fragments and subsequently generated oligomers present a better stability at high potential, showed by Choi and Xu et al[11]. Polymer layer is another effective way to ameliorate the cyclic stability. With the appropriate concentration, aromatic derivatives[12] could form a thin layer on cathode, instead of dimensional growth to short the cell. However, the following reaction at ~ 4.55 V(*vs.* Li/Li$^+$) restricts its further application at higher potential[13].

In recent efforts, we find that the hexamethylene diisocyanate (HDI) exhibits an interesting film-form behavior. HDI is a commercially available product, and has been utilized in various fields such as chemical industry, agriculture and medicine[14]. It also has been investigated as electrolyte additive for SEI film formation at anode[15]. However, to our best knowledge, the promising performance of HDI as cathode film-forming additive was not proposed in literatures. Hence, we will introduce the reaction pathway of film formation and its influence on the electrochemical performance after adding HDI as additive in this work.

The surface of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ charged at 4.6 V(*vs.* Li/Li$^+$) for 3 h in the investigated electrolytes is firstly analyzed with TEM. No obvious precipitated stuff is observed in the electrolyte of 1 M $LiPF_6$ dissolved in PC + DMC(1:1, v/v) as shown in Figure 1a. In the electrolyte with 1 mM HDI, the particle surface almost keeps the same smoothness as the pristine(Figure 1b). When

the HDI concentration increases to 100 mM, some new matters are observed on cathode(Figure 1c), and it accumulates to a ~ 7 nm-thickness layer in the electrolyte with 500 mM HDI(Figure 1d). This physical-existence evidence proves that the surface layer generated from HDI is stable at high potential. If it is uniformly deposited on the cathode surface, this layer should be ~ 1.4 nm thick for the electrolyte with 100 mM HDI, and ~ 0.14 Å thick for the system containing 1 mM HDI. As for EC based electrolyte(Figure 1e, f), no obvious additional layer is identified even in the electrolyte with 500 mM HDI. Since HDI is proved to be stable even at 5 V(vs. Li/Li$^+$)[16] and as shown in Figure S4, this characteristic of solvent dependence probably indicates that this layer should be grown via chemically reaction involved the decomposed species of PC.
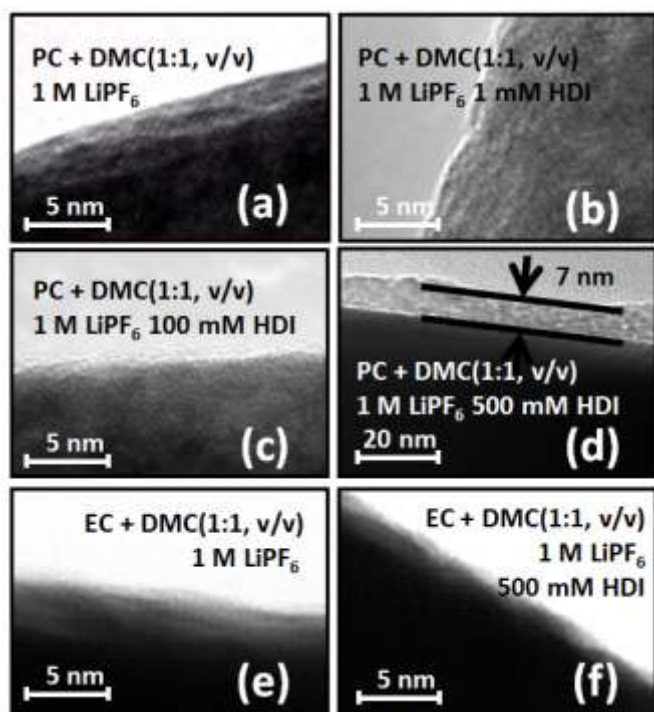

Figure 1. TEM images of LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ electrodes charged at 4.6 V(vs. Li/Li$^+$) for 3 h in PC based electrolytes(a) reference electrolyte, b) with 1 mM HDI added, c) with 100 mM HDI added, d) with 500 mM HDI added) and EC based electrolytes(e) 1 Mol L^{-1} LiPF$_6$ in EC + DMC(1:1, v/v), f) with 500 mM HDI added).

To explore the probable reaction pathway, XPS and FTIR are used to analyze the N-based functional group in the generated surface layer (Figure 2). A new peak related to nitrogen is detected at 401 eV, instead of isocyanate group from pure HDI (399.7 eV). The higher electron binding energy suggests the reduced outer electron density of N atoms, which could be attributed to the formation of amide group[17]. On FTIR spectroscopies, two new peaks are identified at 1526 cm^{-1} and 1751 cm^{-1}, corresponding to the vibrations of N-H and C=O of an amide group. Both results indicate that isocyanate groups should be changed to amide group during polymerization[18]. Additionally, no signal related to nitrogen is detected on the electrode charged in the electrolyte of EC + DMC with HDI.

According to the obtained results and knowledge on organic chemistry, the in-situ generated film should be polymerized along the reaction processes as shown in Scheme 1. Firstly, a PC molecule on electrode surface should be electrochemically oxidative to a cation containing an oxygen free-radical and a positive charged methine in the ends of one onium ion[19]. Free-radicals would dimerize to form peroxide groups, and the charged methines could react with isocyanate groups of HDI via nucleophilic addition to build amide groups[20]. Both addition reactions would form polymer A, in which the peroxide groups and amide groups are bridge-linked. Because peroxide group is unstable, we conjecture that polymer A should be transferred to polymer B via decomposition-reaggregation[21]. Since HDI doesn't form protective layer with EC-based electrolyte under the same condition, we tend to attribute this difference to the absence of methyl protection [19b, 22], which reduces the nucleophilicity of positive charge and lower the activity to react with isocyanate group[23].
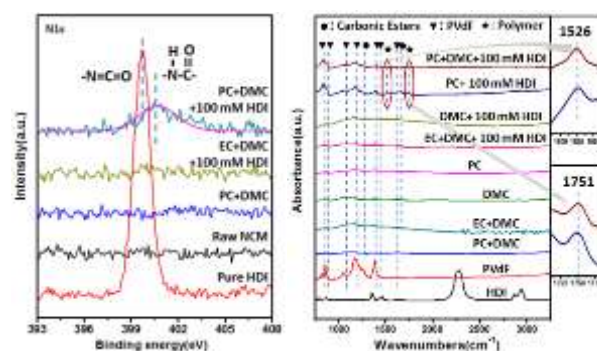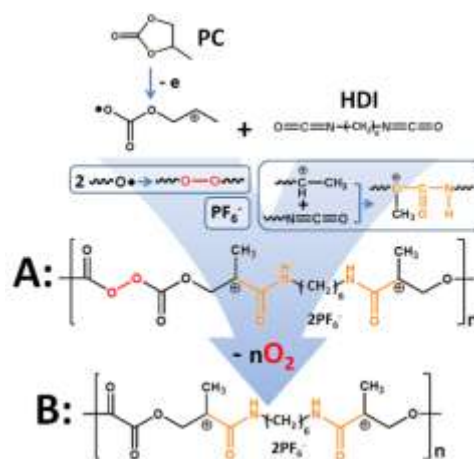

Figure 2. XPS(left) and FTIR(right) spectra of raw material and the surface of LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ cathode after 4.6 V(vs. Li/Li$^+$) - 3 h polarization in different electrolytes.

Scheme 1 Schematic representation illustrating the formation of surface layer via (i) decomposition of PC; (ii) radical polymerization and nucleophilic addition reaction; (iii) decomposition-reaggregation.

The resistances of electrodes after 4.6 V(vs. Li/Li$^+$) - 3 h polarization are tested on a semiconductor parameter analyzer. Since the probe for conductivity test is 50 nm, this measurement should reveal the variation of mono-particle's resistance. As shown in Figure 3a, the tested value in reference electrolyte is 2.8*10^7 kΩ, which is

close to the range of single-particle $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$[24]. After 1 mM HDI is added, the resistance is surprisingly slumped 7 orders to 1.0 kΩ. This significant improvement is probably rooted in the charged methine, in which electrons are easily to accumulate and transport quickly according to quantum tunneling effect. As the increase of HDI concentration, the resistance is gradually enhanced to $\sim 10^8$ kΩ and even higher, indicating that the thick film would retard the kinetics of cathodes due to the improved polarization.

The influence of this protective layer on $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$'s electrochemical performance is evaluated in the coin cells with the electrolyte containing different HDI concentrations tested between 2.5 - 4.6 V(*vs.* Li/Li$^+$). As shown in Figure 3b, $Li/LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ delivers 183 mAh g^{-1} in the reference electrolyte at 0.2 C. The first cycle of charge-discharge curves for the electrolytes with HDI are almost overlapped to that of the control, indicating HDI additive doesn't play any function in the first cycle. $Li/LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ in reference electrolyte is seriously decayed from 181 mAh g^{-1} to 106 mAh g^{-1} after 200-cycle test at 0.5 C(Figure 3c). In the electrolyte containing 1 mM HDI, the discharge capacity at 200th cycle is 149 mAh g^{-1}, 40.6 % higher than that in the reference electrolyte. The capacity fading of the cells are seriously as the increase of HDI concentration. The retained capacity at 100 mM is even lower than the reference system. This variation on cycling performance should be related to interfacial polarization, as shown in Table S1&2 and Figure S3. The cyclic curves are almost overlapped for the systems of the EC-based electroltes with/without HDI (Figure 3d). It further proves that HDI doesn't play a function in the system, which is consistent with TEM results as shown in Figure 1.
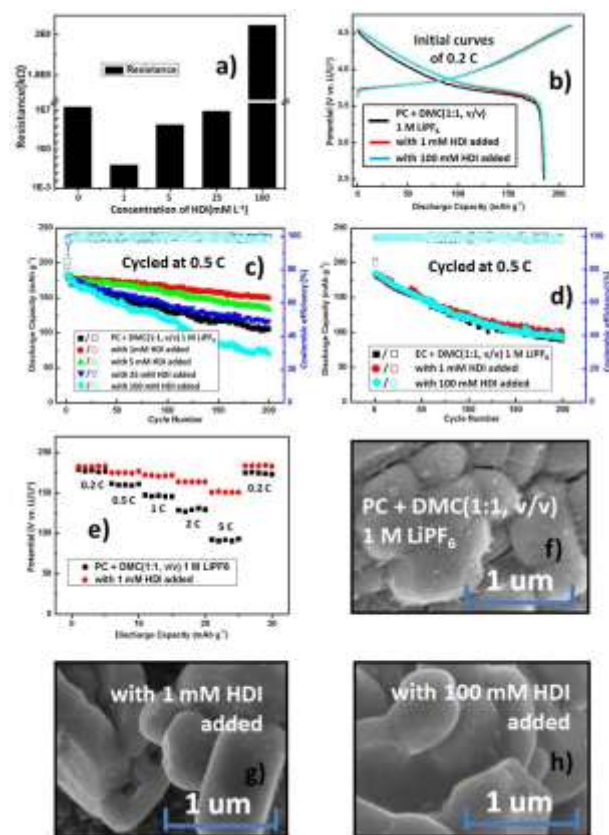

Figure 3. The resistances of cathodes after being charged at 4.6 V(*vs.* Li/Li$^+$) for 3 hours in different concentrations of HDI(a), comparison of the first charge/discharge curves at 0.2 C(b), effects of the additive concentrations on the cycling performance(c) in PC + DMC(1:1, v/v) 1 M LiPF$_6$(c) and EC + DMC(1:1, v/v) 1 M LiPF$_6$(d) between 2.5 - 4.6 V(*vs.* Li/Li$^+$) at 0.5 C, comparison of discharge capacity of electrolytes with and without 1 mM HDI from 0.2 to 5 C (e), and SEM images of cathodes after 200 cycles(f - h).

Also the cell with 1 mM HDI presents the improved rate capability. As shown in Figure 3e, it still keeps 151 mAh g^{-1} under 5 C, and 66.2 % higher than the cell in reference electrolyte. The surface morphologies after cycle are characterized by SEM images(Figure 3f - h & S5). Amorphous sediments are observed on the cathode in reference electrolyte. In contrast, the surfaces of cathode in electrolyte with HDI are much smoother. Obviously, the film constructed from HDI could suppress the electrolyte's decomposition at high potential. To some extent, the building of surface layer would also suppress the particle cracking of LiNi1/3Co1/3Mn1/3O2, as shown in Figure 3f - h & S5.

In summary, we have proved that HDI could build an efficient passive layer to alleviate the side reaction between electrolyte and cathode at high potential. This layer is generated from the directly chemical reaction of HDI and the onium ion oxidative decomposed from propylene carbonate. The optimal system presents a similar discharge capacity at initial cycles, a better rate performance and a more stable rate-retention capability, when compared with the cells without HDI. Our results indicate that HDI could construct a protective layer to widen the working window of practical batteries.

Notes and references

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