

Organic Solvents Containing Zwitterion as Electrolyte for Li Ion Cells

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Imidazolium based zwitterions, 1,2-dimethylimidazolium-3-*n*-propanesulfonate (DMIm-3S) and 1-Butylimidazolium-3-*n*-butanesulphonate (BIm-4S), were synthesized, and utilized them as additive for Li ion cell comprising of graphite anode and LiCoO₂ cathode. The use of 10 wt% of DMIm-3S in 1 M LiPF₆, EC-EMC-DMC (1:1:1 (v/v)) resulted in the increased high rate charge-discharge performance. The low temperature performance of the Li ion cells at about -20 °C was also enhanced by these zwitterion additives. The DMIm-3S additive resulted in the better capacity retention by the Li-ion cells even after 120 cycles with 100% depth of discharge (DOD) at 1 C rate in room temperature. Surface morphology of both graphite and LiCoO₂ electrode before and after 300 cycles was studied by scanning electron microscopy. An analogous study was performed using liquid electrolyte without any additive.

Key Words : Imidazolium based zwitterion additives, Li-ion cell, Liquid electrolyte

Introduction

Recently, a new class of liquid has emerged that consists entirely of ions, so-called ionic liquids. They are made up of two components *i.e.* the anion and cation, and have characteristic properties such as high ion conductivity (over 10⁻² S cm⁻¹), non-flammability, non-volatility and liquidity over a wide temperature range. As both anion and cation can be varied, these solvents can be designed for a particular set of properties such as solubility, density, refractive index, and viscosity.¹⁻⁶ Nguyen *et al.*, reported the physical and electrochemical properties of quaternary ammonium-based ionic liquids.⁷ The favorable and readily tunable physicochemical properties of ionic liquids have led to intense interest in these materials as alternatives to conventional organic media in a range of organic reactions and as new electrolyte solution for batteries in Li-ion battery, fuel cells, and solar cells.⁸⁻¹⁶

Though ionic liquids have their own significance, the mobility of their ions with respect to the potential gradient constrains themselves from achieving the high target ion mass transport. To overcome the ion migration problem, number of research groups have recently designed and synthesized zwitterions as potential ion conductive materials. Since both cation and anion are tethered in a zwitterion, it is expected that the ions cannot migrate with the potential gradient.¹⁷ Extensive study by Ohno group found that an equimolar mixture of lithium salt such as LiTFSI, LiBF₄, and LiClO₄ etc. with various kinds of zwitterions showed only a glass transition temperature *T*_g and established the relationship between *T*_g and ionic conductivity of the zwitterion/lithium salt mixture.¹⁸ Tiyapiboonchaiya *et al.*, also demonstrated the effect of zwitterionic compound 1-butylimidazolium-3-(*n*-butanesulphonate) where the cationic and anionic charges are immobilized on the same molecule, as extremely effective lithium ion dissociation

enhancers⁷. The zwitterion produced electrolyte materials with conductivities up to seven times larger than the pure polyelectrolyte gels.¹⁷ The influence of the TiO₂ nanoparticles and the zwitterionic addition on a poly (Li-AMPS-co-DMAA) polyelectrolyte was also reported.¹⁹ There are many efforts on utilization of zwitterions in Li batteries, and most of the investigations are focused on ionic conductivity of the zwitterions/lithium salt mixture or ion-conductive poly (zwitterion)s.²⁰ However, the additive effect of zwitterions on the performance of Li-ion cell (w.r.s liquid electrolyte system) is far less studied.

In this work, we investigated the effects of zwitterions on the charge-discharge performance at room temperature and low temperature in Li-ion cell comprising of graphite anode and LiCoO₂ cathode. Surface morphologies of both the graphite and LiCoO₂ electrode before and after 300 cycles have also been studied by scanning electron microscopy.

Experimental

1-Butylimidazole, 1,2-dimethylimidazole, 1,3-propanesultone and 1,4-butanedisultone were purchased from Aldrich Chemical Co. Ltd and were used as received for the preparation of zwitterions. The structure of all synthesized materials was confirmed by ¹H-NMR (400 MHz) spectrum using Bruker at 22.6 °C in CD₃OD with tetramethylsilane (TMS) as an internal standard. The thermal stability of the zwitterion additives was analyzed using differential scanning calorimetry TA instruments DSC 2010 with heating rate of 10 °C min⁻¹ from 25 °C to 300 °C.

The electrodes were purchased from the SKC Inc. Korea. Lithium hexafluorophosphate (LiPF₆) was purchased from the Hashimoto Ltd. Japan. The solvents used to prepare the electrolyte were purchased from the Cheil Industries Inc, Korea. The separator was a Celgard 2400 (thickness = 20 μm; porosity = 38%) microporous poly (propylene) (PP)

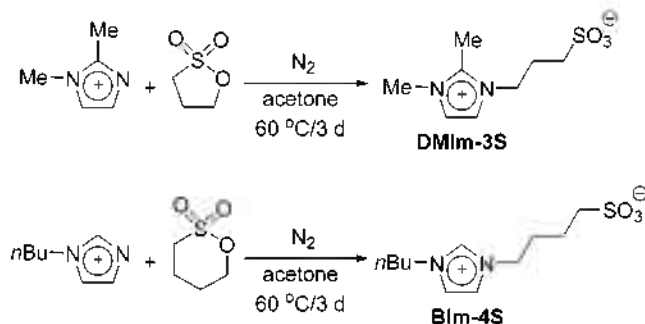
membrane. The full cell configuration was graphite/PP/LiCoO₂ with 10 wt% of the sulfonate containing zwitterion being added to 1 M LiPF₆, EC-EMC-DMC (1:1:1 (v/v)). The electrode area was taken as 3 × 4 cm². They were assembled in the form of aluminium pouch cells. All the above mentioned materials and their assembly were handled inside the dry room and the relative humidity was < 0.5%.

The cyclic voltammogram and the electrochemical stability window were performed with Solartron SI 1286 potentiostat/galvanostat. The cyclic voltammogram was studied for the full cells. The electrochemical stability window was studied using the cells of three – electrode configuration. These cells were employed with Pt-wire (99.99% VWR) as working electrode and Li⁺/Li as the reference electrode. Before being used as the working electrodes, Pt wire wrapped with shrinkable Teflon tube to define geometric surface area, were finely polished with 0.1 μm alumina. The type of cell design used was the dip-type cell where working electrode was Pt wire and no IR compensation was made for the dip-type cell. The fair ionic conductivity of the electrolyte investigated and the compactness of the dip-type cell design were responsible for this consistency.

The impedance characteristics were performed by the electrochemical interface Solartron SI 1260 impedance/gain phase analyzer (Schlumberger). Other electrochemical performances of the Li-ion cells were investigated with Maccor series 4000, USA.

The surface morphology of the electrodes were studied using scanning electron microscopy with a field emission SEM (FE-SEM, Hitachi S-4200) at an accelerating voltage of 15 kV (0.1 kV step⁻¹). YAG single crystal scintillator was used as a detector.

Synthesis of 1,2-dimethylimidazolium-3-*n*-propanesulfonate (DMIm-3S) and 1-butylimidazolium-3-*n*-butanesulphonate (BIm-4S). Zwitterions were synthesized as shown in Scheme 1.²¹ To a solution of 1,3-propanesultone (0.035 mol) in acetone (40 mL), 1,2-dimethylimidazole (0.035 mol, 3.43 g) was added at room temperature. The reaction mixture was stirred under N₂ atmosphere for 3-4 days at 60 °C during which the product slowly formed as a white precipitate. The precipitate was filtered and washed with acetone under nitrogen, and dried under vacuum to give DMIm-3S as a hygroscopic white powder. Similarly, BIm-



Scheme 1. Synthesis of 1,2-dimethylimidazolium-3-*n*-propanesulfonate (DMIm-3S) and 1-butylimidazolium-3-*n*-butanesulphonate (BIm-4S).

4S was also synthesized using 1-butylimidazole and 1,4-butanedisulfone. DMIm-3S: ¹H NMR (CD₃OD) δ 7.58 (d, *J* = 2.04 Hz, 1H, CH_a), 7.49 (d, *J* = 2.04 Hz, 1H, CH_b), 4.38 (t, *J* = 7.36 Hz, 2H, CH₂), 3.84 (s, 3H, CH₃), 2.85, (t, *J* = 6.93 Hz, 2H, CH₂), 2.67 (s, 3H, CH₃), 2.27 (m, 2H, CH₂). BIm-4S: ¹H NMR (400 MHz, CD₃OD) δ = 9.06 (s, 1H, CH), 7.68 (d, *J* = 1.78 Hz, 1H, CH_a), 7.66 (d, *J* = 1.68 Hz, 1H, CH_b), 4.25 (m, 4H, 2N-CH₂), 2.85 (t, *J* = 7.45 Hz, 2H, CH₂), 2.06 (m, 2H, CH₂), 1.89 (m, 2H, CH₂), 1.78 (m, 2H, CH₂), 1.38 (m, 2H, CH₂), 0.99 (m, 3H, CH₃).

Results and Discussion

Two different imidazolium-based zwitterion-type compounds, DMIm-3S and BIm-4S, were synthesized according to the method reported by Ohno *et al.*,²¹ and used them as electrolyte additives for full cell Li-ion battery comprising graphite/PP/LiCoO₂ with 1 M LiPF₆, EC-EMC-DMC (1:1:1 (v/v)). As shown in Figure 1(A), the novel zwitterion DMIm-3S bearing propanesulfonate appendage and 1,2-dimethyl groups on imidazolium ring showed high glass temperature (*T*_g = 163 °C) and melting temperature (*T*_m = 243 °C) than the known zwitterion BIm-4S (*T*_g = 62 °C, *T*_m = 136 °C) in Figure 1(B). The observed *T*_m of BIm-4S was slightly lower than the reported *T*_m (158 °C).²⁰ The higher *T*_g and *T*_m values of the DMIm-3S having propanesulfonate

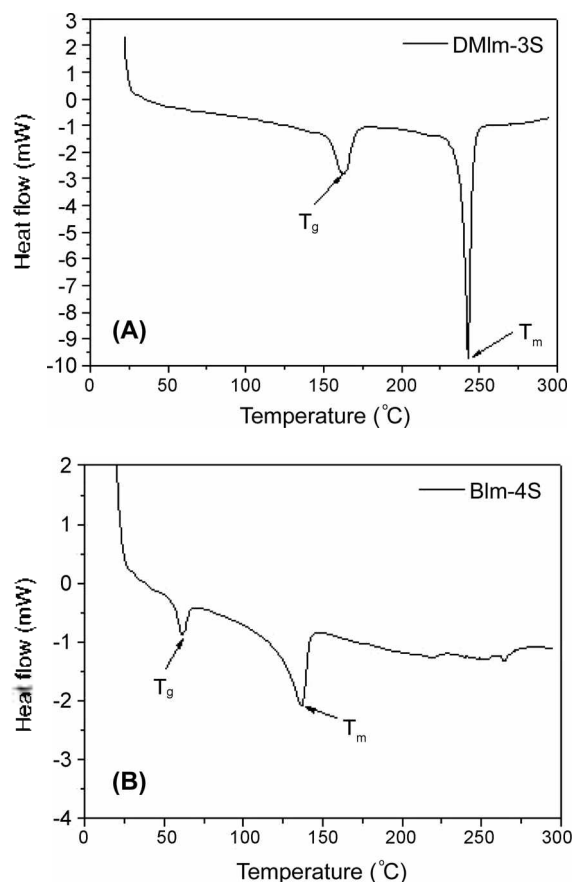


Figure 1. DSC charts of the zwitterions DMIm-3S (A) and BIm-4S (B).

appendage may be due to the lower freedom compared with the BIm-4S with longer alkyl butanesulfonate appendage. Although these zwitterions have high T_m values, it has been known that the zwitterion/lithium salt mixture exhibited ionic conductivity¹⁸ and BIm-4S act as a lithium ion dissociation enhancer in Li-polymer electrolytes.¹⁷ Therefore, it is considered that liquid domain may not be affected by the addition of appropriate amounts of zwitterion into the liquid electrolyte composed of 1 M LiPF₆, EC-EMC-DMC (1:1:1 (v/v)), and would increase the ionic conductivity resulting in the positive effect on the performance of Li-ion full cell.

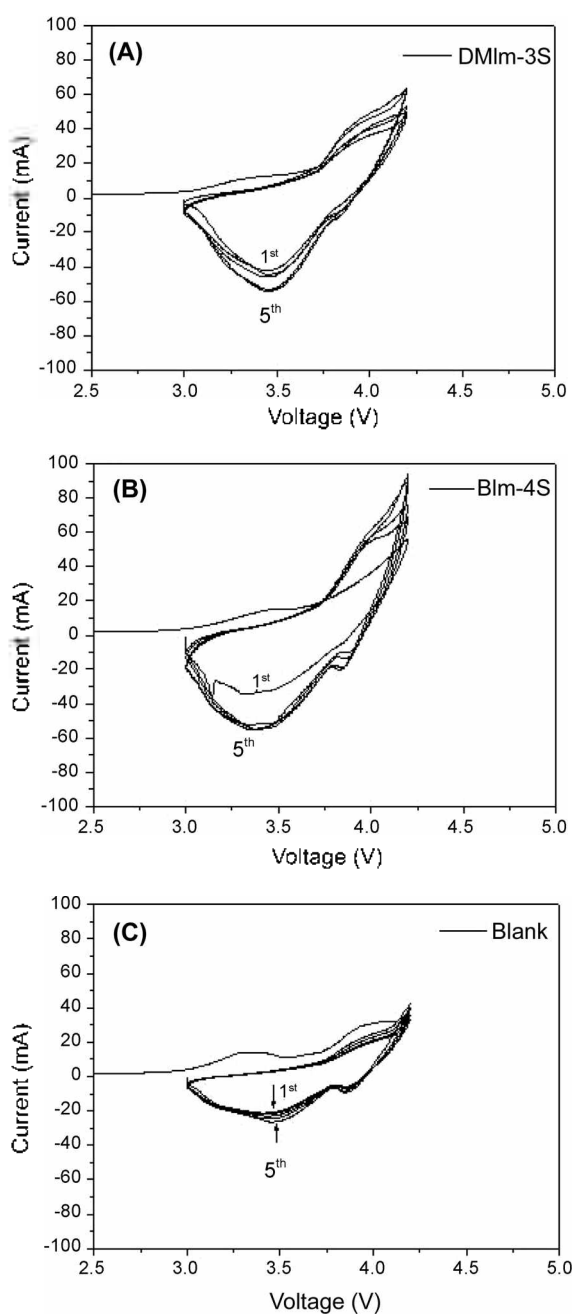


Figure 2. Cyclic voltammograms (CV) with 10 wt% zwitterion additive DMIm-3S (A), BIm-4S (B), and without any additive (C) in a 1M LiPF₆, EC-EMC-DMC (1:1:1 (v/v)) at a scan rate of 1 mVs⁻¹ for about 5 cycles.

The full cells have been assembled using graphite/PP/LiCoO₂ configuration with the electrolyte system being 1 M LiPF₆, EC-EMC-DMC (1:1:1 (v/v)) containing 10% of the DMIm-3S, and measured of their cyclic voltammogram (CV). The CV measurement for the full cell was started at open circuit potential (normally; OCP = 0.0 V). A scan rate of 1 mVs⁻¹ was used to sweep both for charging and discharging the cell, from 0 V to 4.2 V and 4.2 V to 3 V respectively. The CVs of such cells with 10 wt% DMIm-3S and BIm-4S additives are shown in Figure 2(A) and (B), respectively, and Figure 2(C) shows the CV for the 0 wt% zwitterion additive. The anodic peak current values of blank, BIm-4S and DMIm-3S were found to be 40 mA, 90 mA and 60 mA, respectively. The cathodic peak current values of blank, BIm-4S and DMIm-3S were found to be 30 mA, 50 mA and 60 mA, respectively. In case of both BIm-4S and DMIm-3S, the anodic and cathodic peak current values increased appreciably for the first five cycles than that of the blank electrolyte. Even though the anodic and cathodic peak current values of DMIm-3S are lower than that of BIm-4S, the better cycling performance was observed for DMIm-3S. This may be due to the formation of more stable Solid Electrolyte Interface (SEI) compared to that of BIm-4S.

The room temperature performance of the Li-ion cells with and without zwitterion additives was carried out for about 5 cycles at 1/3 C rate. Figure 3(A) clearly exhibits that

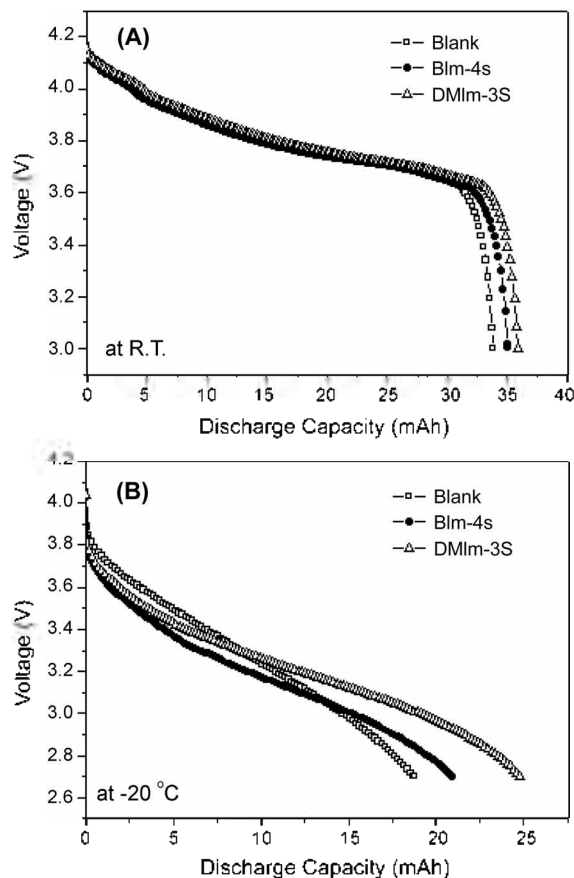


Figure 3. Discharge performance of the graphite/PP/LiCoO₂ cell at 25 °C (A) and at -20 °C with the 1/3 C rate (B).

the 10 wt% of DMIm-3S in 1M LiPF₆. EC-EMC-DMC (1:1:1 (v/v)) shows comparatively better room temperature performance. All these Li-ion cells were also investigated of their low temperature performance at -20 °C. The cells were applied with the same C rate as for the room temperature performance. The cut-off voltages during charge and discharge of these cells were found to be 4.2 V and 2.7 V respectively. The electrolyte consisting of 10 wt% of either of the zwitterions synthesized showed a better performance than that of the blank electrolyte. Figure 3(B) shows a clear perspective on the low temperature performance of the Li-ion cells. From Figure 3(B), the discharge capacity of the electrolyte with DMIm-3S additive at -20 °C is found to be 25 mAh. Wherein, the discharge capacities for blank and the electrolyte with BIm-4S are found to be similar say 21.25 and 18.75 mAh, respectively. The better low temperature performance of the Li ion cells may be due to the Li-ion dissociation ability of the zwitterion additives.¹⁷

Each cell with the electrolyte containing 0 wt% and 10 wt% of DMIm-3S zwitterion was also investigated with different C rates such as 0.5C, 1C, 2C, and 3C. As shown in Figure 4(B), addition of a zwitterion DMIm-3S exhibited similar performance, even at different C rates, to that of electrolyte solution without zwitterion additives in Figure 4(A). This figure depicts the variation in discharge voltage

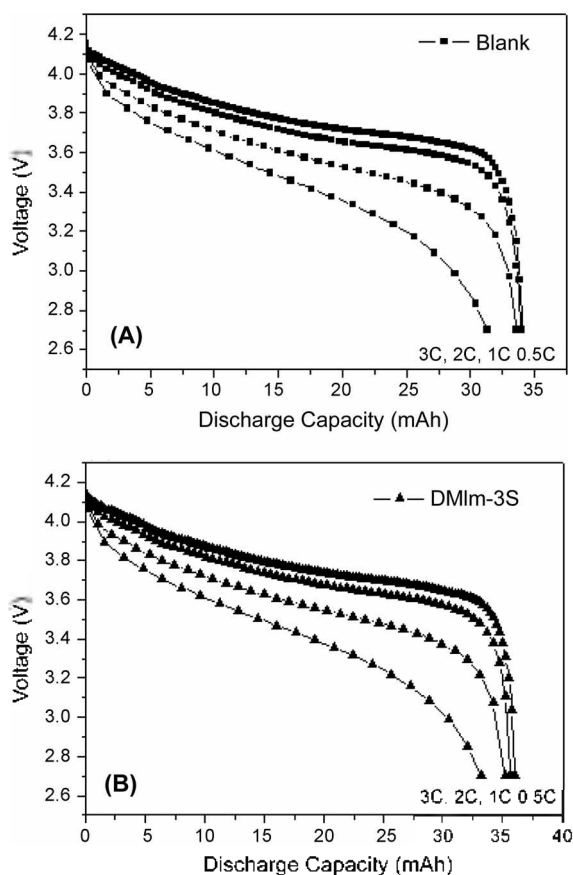


Figure 4. Discharge characteristics with different C-rates such as 0.5C, 1C, 2C, 3C at 25 °C for 1 M LiPF₆. EC-EMC-DMC (1:1:1 (v/v)) without any zwitterion additives (A) and with 10 wt% of DMIm-3S additive (B).

profiles at different C rates such as 0.5C, 1C, 2C and 3C. The discharge capacity of the electrolyte with DMIm-3S additive at 3C rate and cut off voltage (2.7 V) is found to be 33.11 mAh and without any zwitterion additive at the same rate and cut off voltage is obtained as 31.34 mAh. Similar performance was observed with respect to other C rates. Hereby, these results clearly suggest the positive effects of the zwitterion additive on the Li ion cell performance.

We next investigated the electrochemical stability window for the electrolytes containing 0 wt% or 10 wt% of either of these zwitterions. It is well known factor that the electrolyte having a wider potential window is most preferable for practical purposes.²² In Figure 5, the electrochemical stability window range was from -0.107 V to 5.25 V for the electrolyte containing 10 wt% of DMIm-3S proving it wider than that of the other electrolytes used in this study. At lower potential ranges (0 V), electrochemical reaction causing Li plating and stripping (redox reaction) occurs whereas at higher potential ranges (5 V), electrochemical reactions favoring electrolyte decomposition occurs. The electrolytes containing each of the zwitterion additives are electro-

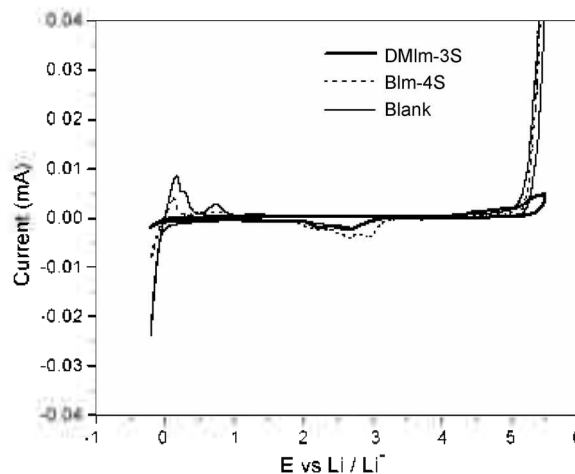


Figure 5. Electrochemical stability window for the electrolytes with no additive (blank), 10 wt% DMIm-3S, and 10 wt% BIm-4S.

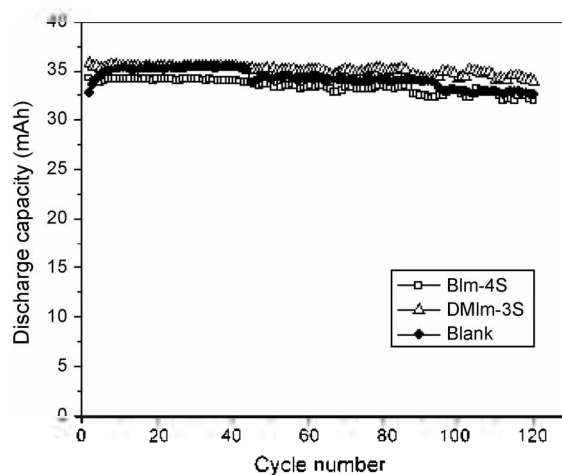


Figure 6. Cycling performances of the electrolytes with and without 10 wt% zwitterion additives.

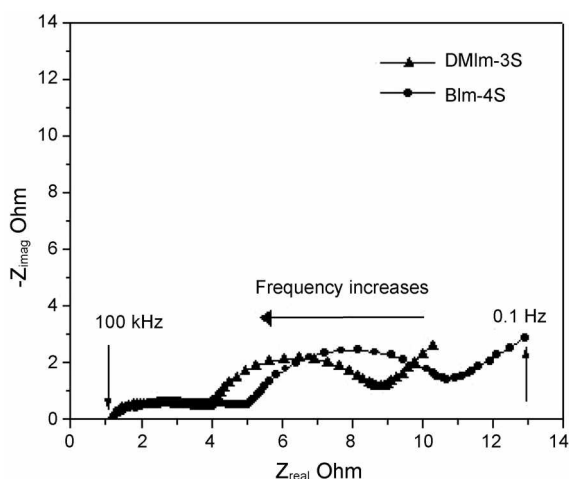


Figure 7. Impedance spectra for liquid electrolyte with 10 wt% zwitterion additives at 25 °C in the frequency range of 100 kHz to 0.1 Hz.

chemically stable in the potential range of 3.0 V–4.2 V. It is thereby, crystal clear that the lithium intercalation and deintercalation is not affected by the addition of zwitterions to the liquid electrolyte system. The Li-ion cells with and without zwitterion additives were allowed to run for more than 120 cycles at 1C rate. Figure 6 clearly depicts the cycle life of each Li-ion cell. The discharge capacity retention of the cells containing DMIm-3S additive, BIm-4S additive and blank electrolyte was 96.83%, 91.4% and 93.26%, respectively.

The impedance characteristics were analyzed after 180 cycles for the Li ion cells with liquid electrolyte containing

zwitterion additives. The impedance spectra were measured for each cell after its fully charged state (OCV = 4.2 V) at 25 °C. It has a small loop followed by a larger loop in the frequency range of 100 kHz to 0.1 Hz. The first smaller loop is assigned to the graphite anode/electrolyte interface and the second larger loop is assigned to the LiCoO₂ cathode/electrolyte interface.^{33,34} From Figure 7, it may be understood that the electrolyte containing BIm-4S exhibits an increased interfacial resistance than that of the electrolyte containing DMIm-3S additive. This may be directly correlated with that of the capacity fade during cycle life test.

To understand the effect of the zwitterionic salt type additive on the surface morphology of the electrodes, we undertook a scanning electron microscopy (SEM) study. Figure 8(A) shows the surface of an uncycled graphite anode. Figure 8(B) and (C) shows the graphite anode which was allowed to undergo over 300 cycles with 0 wt% and 10 wt% of DMIm-3S additive, respectively. In Figure 8(B), some non-graphitic aggregates were observed on the surface of graphite anode. These might have been the so called dendrite growth which could lead to the sudden drop in Li-ion cell performance. In Figure 8(C), there are no such non-graphitic aggregates present on the surface of the anode. These exfoliations occurred only at the edges of the anode due to increased current density. Such exfoliations may be due to the liberation of gases favored by the zwitterion additive, DMIm-3S. In spite of such exfoliations, the cycling performances of the electrolyte solution with 10 wt% DMIm-3S additive surpassed that of the blank electrolyte.

Figure 9(A) shows the surface of an uncycled LiCoO₂. Figure 9(B) and (C) shows the SEM images of LiCoO₂

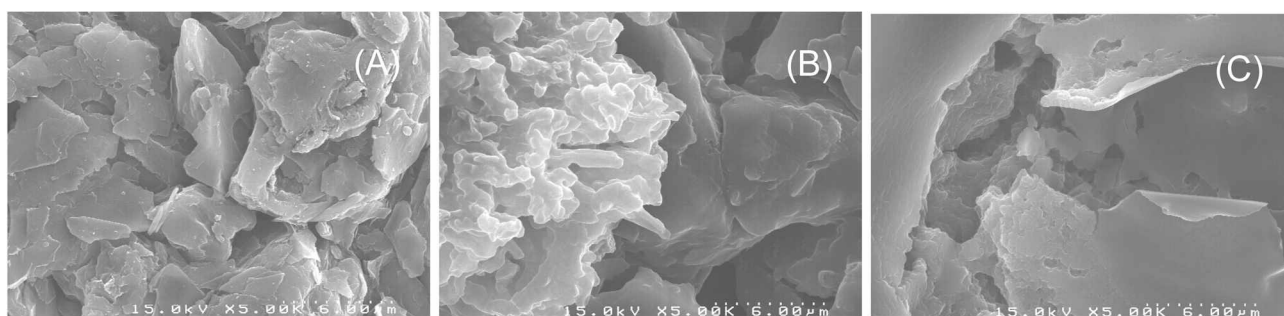


Figure 8. Scanning electron microscopy (SEM) images of an uncycled graphite anode (A), and graphite anode that has undergone over 300 cycles without zwitterion additive (B) and with 10 wt% of DMIm-3S additive (C).

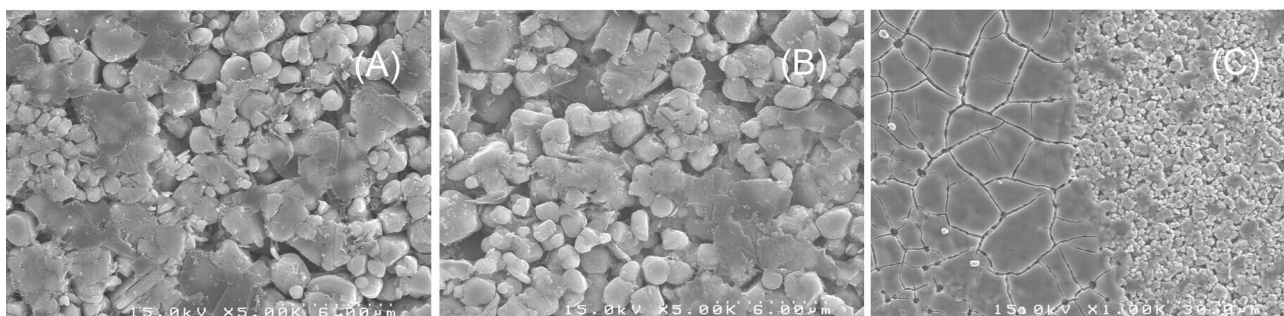


Figure 9. Scanning microscopy (SEM) images of an uncycled LiCoO₂ electrode (A) and electrodes that has undergone over 300 cycles without (B) and with 10 wt% of DMIm-3S additive (C).

cathode which was cycled over 300 cycles with 0 wt% (B) and 10 wt% (C) of DMIm-3S additive. Figure 9(C) shows that the film formed on the surface of the cathode was not uniform, whereas the LiCoO₂ cathode did not result in any non-uniform film formation on its surface shown in Figure 9(A). In spite of the formation of such non-uniform film, the electrode exhibited stable behavior and better cycling performances with 95% capacity retention for more than 120 cycles.

Conclusion

Our current focus is on the electrolyte phase which continues to occupy the central role in Li-ion battery performance and stability. Among the inorganic additives that are widely focused by the battery researchers, such organic additives form a new era in the electrochemical devices. In this study, we observed that the electrolyte which contained the zwitterion additive DMIm-3S increased the high rate performance, room temperature as well as low temperature performance significantly. The cycle life test also revealed that the DMIm-3S additive added electrolyte showed similar capacity retention to that of the blank electrolyte solution. The progressive study on the interfaces and the effects of the electrolyte with and without zwitterion additives is likely to result in superior lithium-ion batteries in the near future.

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