Short communication

A study of tri(ethylene glycol)-substituted trimethylsilane (1NM3)/LiBOB as lithium battery electrolyte ☆

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ABSTRACT

Silicon-based electrolyte has emerged as a primary candidate for the development of large lithium-ion batteries for electric vehicle (EV) and other systems in which safety is a primary consideration. Comparing to the electrolyte used in the conventional lithium-ion batteries, which are flammable, volatile, and highly reactive organic carbonate solvents, silicon-based electrolytes are thermally and chemically stable, less flammable and environmental benign. Tri(ethylene glycol)-substituted trimethylsilane (1NM3) was identified as a focus of investigation due to its high conductivity and low viscosity. We present the results of a systematic investigation of the 1NM3-based electrolytes with lithium bis(oxalate)borate (LiBOB) salt, including temperature dependent ionic conductivity and lithium cell performance. Lithium-ion cell with $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ as the positive electrode and MAG graphite as the negative electrode has shown excellent cyclability using 1NM3-LiBOB as electrolyte.

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1. Introduction

Numerous attempts have been made to improve the thermal stability and safety characteristics of the electrolytes in lithium-ion battery in the last two decades. Silicon-based electrolyte has emerged as a primary candidate for the development of rechargeable lithium-ion battery in application such as implantable medical device, electric vehicles (EV), and hybrid electric vehicles (HEV) in which safety is a primary consideration [1]. Comparing to the electrolytes used in the conventional lithium-ion batteries, which are flammable, volatile, and highly reactive organic carbonate solvent, silicon-based electrolytes are thermally and electrochemical stable, less flammable and environmental benign. By overcoming the disadvantages of poly(ethylene glycol) (PEG)

as polymer electrolytes, such as electrochemically instability and crystallization at room temperature [2], polysiloxanes have been conjugated to PEG in order to improve its conductivity and physical properties, thus (ethylene glycol)-functionalized polysiloxane electrolytes have become one of the most popular majors in silicon-based electrolytes. These approaches were investigated by Watanabe, Smid, Shriver and others more than two decades ago [3–6]. However, their polymers, when doped with lithium salts, were only modest electrical conductors, with ambient conductivities $\sigma \approx 10^{-4}\,S\,cm^{-1}$ [3,7]. For commercial applications, conductivities of at least $10^{-3}\,S\,cm^{-1}$ are needed. Recently, the oligo(ethylene glycol)-functionalized silane electrolyte solvent was found to dissolve most lithium salts easily and showed a comparable ionic conductivity ($10^{-3}\,S\,cm^{-1}$) at room temperature to that of conventional organic carbonate-based electrolytes. Tri(ethylene glycol)-substituted trimethylsilane (1NM3) was identified as a focus of interest due to its well-balanced properties: high conductivity and low viscosity when it was used as a non-aqueous electrolyte [8].

Though the conductivity and solvation kinetics of lithium salts in oligo(ethylene glycol)-functionalized silane electrolyte were investigated [7], only scattered cell performance evaluations of the 1NM3 electrolyte are known. A half cell cycling performance test (Li/0.8 M LiBOB-1NM3/$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA)) at room temperature was reported and the cell cycled well and showed no capacity fade up to 80 cycles [8]. At the same time, it was found
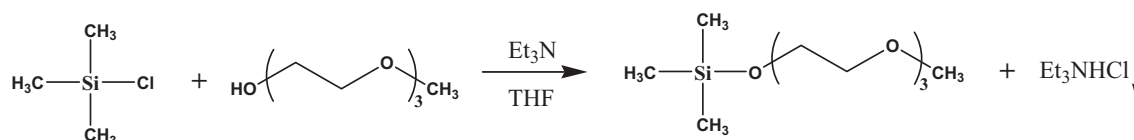
Fig. 1. Schematic synthesis route for tri(ethylene glycol)-substituted silane (1NM3).

that a full cell performance test with $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ as the positive electrode and MCMB graphite as the negative electrode had shown excellent cyclability at elevated temperature (40 °C) [8]. In both cases, no cell performance evaluation was made with $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ (NCM) cathode and graphite (MAG) anode when 1NM3 was used as the electrolyte. NCM and MAG are both commercial electrode materials and widely used in the state-of-the-art rechargeable lithium-ion battery industry. We believe the studies of the cells using these electrodes are important towards to the further understanding of the role of silane materials as electrolytes in lithium-ion battery.

A series of studies had been made in our group at Argonne National Laboratory to enable the silane based electrolyte towards the next generation electrolyte in EV/HEV applications from the support and funding from the lithium ion battery industry. LiBOB salt was found to be very suitable in the silane electrolyte, because it doesn't contain labile fluorine and is thermally stable. It can also provide a passivation film on a graphite anode [9,10]. In this work, we have undertaken the evaluation of using LiBOB as well as other lithium salts in 1NM3 as the electrolyte in NCM/MAG cell system.

2. Experimental

2.1. Materials and apparatus

Tri(ethylene glycol) monomethyl ether (95%), chlorotrimethylsilane (99.0%), triethylamine (99.5%), and THF (99.9%, anhydrous) were purchased from Aldrich and dried over molecular sieves before use. Lithium hexafluorophosphate ($LiPF_6$) (99.9%) and lithium bis(oxalate)borate (LiBOB) (99.87%) were purchased from Novolyte. Lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) (99.95%) was purchased from Sigma–Aldrich. Lithium difluoro(oxalato)borate (LiDfOB) was supplied by Central Glass Co., Ltd. All lithium salts were used as received. $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ (NCM) cathode and MAG graphite anode electrodes were obtained from EnerDel Inc. The active materials loading were 13 mg cm^{-2} for NCM cathode. The active loading of MAG graphite anode was paired with its corresponding cathode.

The synthesized 1NM3 sample was analyzed by NMR and FTIR to identify the impurity. ^{1}H NMR analysis of the sample was carried out on a Bruker 500 MHz FT NMR spectrometer. FTIR measurement of the sample was obtained on a Perkin-Elmer Spectrum 100. Ionic conductivity was determined by YSI 3200 Conductivity Instrument equipped with an YSI 3253 conductivity cell. The conductivity was recorded over a temperature range from −20 to 80 °C.

The charge–discharge cycling performance was tested on a Maccor Electrochemical Analyzer using 2032 coin cells with NCM as the cathode, MAG graphite as the anode, and a microporous polyethylene/polypropylene/polyethylene separator. The effective electrode area was 1.6 cm^2 and the cell capacity is determined by the cathode electrode. A two-cycle formation step was applied prior to the cycling test at the C/5 rate. Performance data were acquired and analyzed by the software associated with the instrument.

2.2. Synthesis

The silane solvent 1NM3 was synthesized according to ref. [11] with a modified scale-up procedure (Fig. 1). Chlorotrimethyl-

silane (329.2 g, 3.03 mol) was added dropwise to a solution of triethylene glycol monomethyl ether (451.6 g, 2.75 mol) and triethylamine (306.6 g, 3.03 mol) in THF (1.0 L) with ice-water bath. Mechanical stirring was used due to the high viscosity of the mixture and an inert atmosphere (Argon) was used to prevent moisture. The reaction mixture was kept on stirring at room temperature for 12 h after complete addition. The reaction was followed with FT-IR by frequent sample measurements until no −OH absorbance (∼3400 cm^{-1}) was detected. The solution was then filtered. THF and unreacted materials were removed by rotary evaporator prior to the vacuum distillation. A colorless liquid (yield 80%) was obtained for the fraction with boiling point of 60–63 °C/0.2 mmHg.

3. Results and discussion

3.1. 1NM3-lithium salts: conductivities and cycling performance

The silane solvent 1NM3 has a high boiling point and a low viscosity [8]. It can easily dissolve most of the lithium salts, such as LiBOB, LiDfOB, $LiPF_6$, $LiBF_4$, and LiTFSI to form liquid electrolytes. The ionic conductivities of the selected lithium salts-1NM3 electrolytes as a function of temperature are shown in Fig. 2a. The nonlinear (curved) profile indicates that their conductivity–temperature relationships do not follow the Arrhenius equation. Instead, the Vogel–Tammann–Fulcher (VTF) can be applied to describe the temperature-dependent conductivity of the complex system

$$\sigma(T) = \sigma_0 T^{1/2} \exp[-E_a/R(T - T_0)]$$

where σ_0 is the pre-exponential factor proportional to $T^{-1/2}$ and T_0 is the temperature at which the transport function ceases to exist or the solvent structural relaxation becomes zero and may be regarded as the glass transition temperature. It is interesting that the conductivity behavior of the oligomer compound (1NM3) still falls into the empirical VTF equation [2,11], which is normally valid for polymer and glassy electrolytes, or concentrated electrolyte solutions [12]. According to the VTF equation, $\ln(\sigma T)$ should have a linear relationship with $(T - T_0)^{-1}$. Using the T_0 values in Table 1, the $\ln(\sigma T)$ versus $(T - T_0)^{-1}$ plots were established and fit well linearly (Fig. 2b).

As seen in Table 1, the prefactor, σ_0, might be related to the number of mobile charge carriers in the system [13], which lies in the order of $LiPF_6$ > LiBOB > LiTFSI. It seems to be in the same order of the average ion mobility of lithium salts [1]. The term B can be thought of as the energy barrier for the rotational motion of oligomer or polymer segments [13], and the value of that is following the order of $LiPF_6$ > LiBOB > LiTFSI. The lower energy barrier when using LiTFSI as a salt may be due to the fact that LiTFSI favors solvents with a

Table 1
Fitting parameters of VTF equation to the temperature-dependent conductivities of 1NM3 electrolytes.

Electrolyte	Concentration	T_0/K	E_a/kJ mol^{-1}	σ_0/S cm^{-1}
1NM3-LiTFSI	0.8M	202	1.08	0.115
1NM3-LiBOB	0.8M	196	1.36	0.146
1NM3-LiPF$_6$	0.8M	192	1.90	0.256

Fig. 3. Cathode specific capacity versus cycle number for NCM/1NM3-Li Salts/MAG cells at 25 °C.

trode (MAG) for the cell using LiPF$_6$ or LiTFSI in 1NM3 electrolyte might be problematic. Given the fact that LiDfOB is a not a commercial available salt, LiBOB seems to be the best lithium salt candidate for the silane electrolyte.

3.2. Optimization of 1NM3-LiBOB electrolyte

It is of great interest to carry out more detailed investigations to illustrate the optimization of 1NM3-LiBOB as the electrolyte for these state-of-the-art commercial electrode materials. Therefore, the ionic conductivity, cycling performance, upper voltage stability, and rate capability of the electrolyte with 1NM3-LiBOB were selected for the following study.

3.2.1. Ionic conductivities of 1NM3-LiBOB with various concentrations

The conductivities of the 1NM3-LiBOB with different concentrations were measured as a function of temperature (−20 to 80 °C). Plots of conductivity against temperature (log σ versus 1000/T) for the 1NM3 electrolyte are shown in Fig. 4. As expected, a non-linear Arrhenius behavior of the conductivity of 1NM3-LiBOB complexes in the given temperature range was observed, suggesting that besides electrical transport by an ion-hopping mechanism, oligomeric ethylene glycol segmental motion also contributes to the conductivity [2]. Accordingly, VTF equation has been used
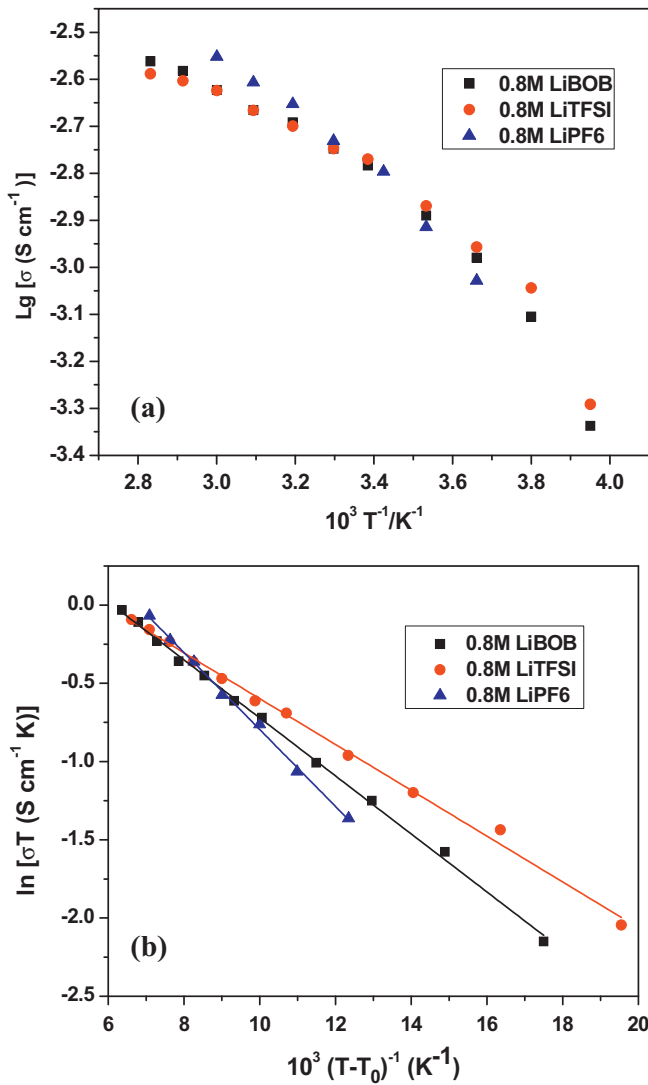

Fig. 2. (a) Arrhenius plots of conductivity versus temperature for 1NM3 with various lithium salts at 0.8 M concentration. (b) Vogel–Tammann–Fulcher (VTF) plots of conductivity versus temperature for 1NM3 with various lithium salts at 0.8 M concentration.

low dielectric constant ($\varepsilon_{1NM3} = 5.13$), which makes it an interesting salt to be investigated for the polymer/oligomer based electrolytes [14]. The fitting parameter T_0 of each lithium salts follows an order of LiPF$_6$ < LiBOB < LiTFSI. The value of T_0 in 1NM3-LiTFSI electrolyte is also consistent with the reported value (206 K with 1.25 M concentration) [11]. Since T_0 values are usually observed lie 50 K below the glass transition temperature T_g [15], we may be able to predict their T_g would have the same trend as the values of T_0 against the salt selections.

Fig. 3 shows the cycling performance of the above electrolytes in NCM/MAG cells cycled between 2.7 and 4.1 V with a constant current of 0.4 mA at room temperature. The electrolytes used were LiPF$_6$, LiTFSI, LiBOB, and LiDfOB in 1NM3 with the same concentration (0.8 M). Despite an observable irreversible capacity occurred during the first cycle, the cell using LiBOB or LiDfOB in 1NM3 as the electrolyte shows good cycling performance due to the passivation film formed on the graphite anode surface by the reductive decomposition of the lithium salts. While the cell used 1NM3-LiPF$_6$ or 1NM3-LiTFSI as the electrolyte, significant capacity fading was observed with 80% loss even after first 3 cycles. The lack of solid electrolyte interface (SEI) film on the surface of the negative elec-
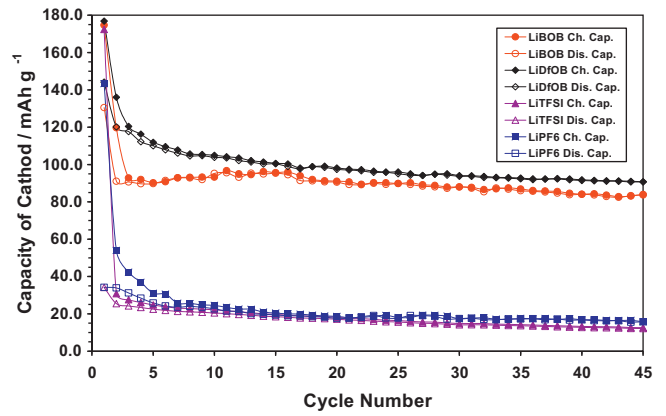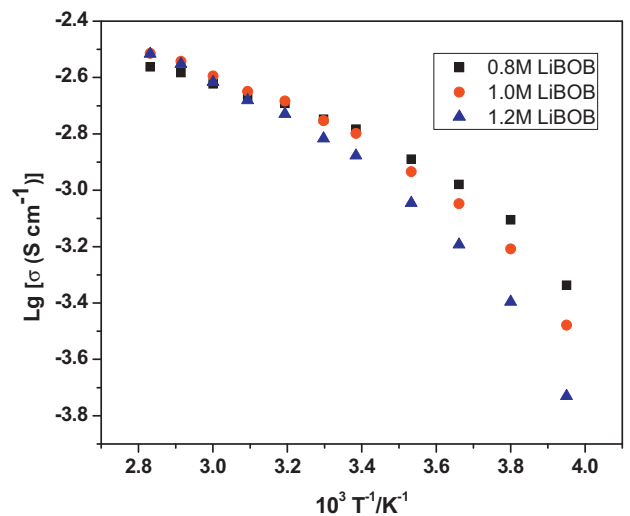

Fig. 4. Arrhenius plots of ionic conductivity for 1NM3 electrolyte with various LiBOB concentrations.

Table 2
Fitting parameters of VTF equation to the temperature-dependent conductivities of 1NM3-LiBOB electrolytes.

| Electrolyte	Concentration	T_0/K	E_a/kJ mol^{-1}	σ_0/S cm^{-1}
	0.8M	196	1.36	0.146
1NM3-LiBOB	1.0M	193	1.82	0.224
	1.2M	193	2.25	0.311

to fit to the behavior the temperature-dependent conductivities of 1NM3, which couples cation mobility to oligomeric segmental motion. The activation energy (E_a) and the ideal glass transition temperature (T_0) could be determined using the VTF equation (Table 2). As the lithium concentration increased, the prefactor, σ_0, should also increase since it might be related to the number of mobile charge carriers in the system [13]. The value of energy barrier B is also predicted to increase monotonously as the concentration of the lithium salt rises as is also the case for this system [13,16]. It can be seen in Fig. 4 that 0.8 M LiBOB in 1NM3 electrolyte has the highest conductivity (~1.7 mS cm^{-1}) at room temperature (25 °C). At low temperature, the slope versus the reciprocal of the temperature increases greatly, indicating the high activation energy for the ion transportation for 1NM3-LiBOB, which is attributed to the combined effect of salt dissociation and solution viscosity [17].

3.2.2. Cycling performance of 1NM3-LiBOB

Fig. 5 shows the cycling performance of lithium-ion cells Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ (NCM)/MAG graphite with 0.8 M, 1.0 M, and 1.2 M LiBOB in 1NM3. Cells were charged and discharged at a $C/5$ rate and cycled between 3.0 and 4.1 V. All cells cycled extremely well with 100% efficiency and showed fairly stable capacities. To our surprise, the cell with 0.8 M LiBOB in 1NM3 electrolyte shows less capacity and stability than that of 1.2 M LiBOB in 1NM3 electrolyte, which is inconsistent with their room temperature ionic conductivities since higher conductivity electrolyte facilitates ion transport during the charge/discharge cycle in lithium-ion battery. An attempted explanation has been made based on the fact of a large amount of LiBOB was anticipated to provide an effective passivation film on the graphite anode surface during the first charging process [18–20]. Considering typically less than 0.4 mL electrolyte was used in each 2032 coin cell, the consumption of LiBOB salt could be significant in the cell. The 1NM3-LiBOB electrolyte with lower concentration might not be able to maintain sufficient salt concentration after the formation of the passivation film during the first cycle. In the viewpoint of cell performance, the optimized concentration of LiBOB in 1NM3 is 1.2 M.
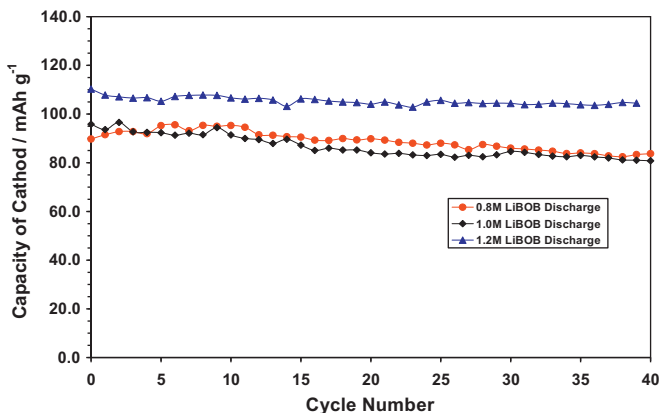
Fig. 5. Cathode specific capacity versus cycle number for NCM/1NM3-LiBOB/MAG cells with various LiBOB concentrations at 25 °C.
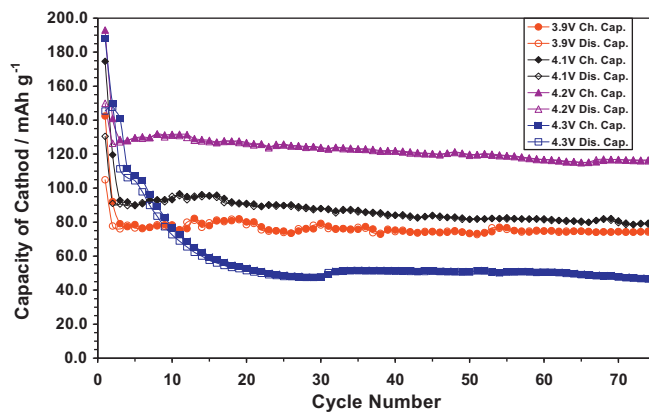

Fig. 6. Cathode specific capacity versus cycle number for NCM/1NM3-LiBOB/MAG cells with different upper cutoff voltages.

3.2.3. Upper cutoff voltage of 0.8 M 1NM3-LiBOB

Fig. 6 shows the capacity retention of the above NCM/MAG cells cycled at room temperature with a constant current of 0.4 mA. The electrolyte used was 0.8 M LiBOB in 1NM3. When the cell was cycled between 2.7 and 3.9 V, the cell performed extremely well with 100% efficiency and showed no capacity fade after 100 cycles. When the cell was cycled over 2.7–4.1 V or 2.7–4.2 V, the cell showed slow capacity fading, which is acceptable under the lower concentration (0.8 M) electrolyte condition. When the upper cutoff voltage of the cell was increased to 4.3 V, the cell showed severe capacity fading, with almost 50% fading after only 10 cycles. The capacity fading is due to the upper voltage limit (4.5 V) of LiBOB salt as reported when an inert electrode (platinum) was used [21]. Nevertheless, the upper voltage limit of the 1NM3-LiBOB (4.2 V) is higher than our previous results of disiloxane (2SM3)-LiBOB system (4.0 V) [22].

3.2.4. Rate capability of 1NM3-LiBOB electrolyte

The rate capabilities of 1NM3-LiBOB electrolyte were evaluated by charging a NCM/MAG lithium-ion cell with a constant current equivalent to $C/10$ to 4.1 V, followed by a constant voltage charge until a cutoff current equivalent to $C/20$. The cell was then discharged to 2.7 V at constant currents of $C/20$, $C/10$, $C/5$, $C/2$, C, and $2C$. As shown in Fig. 7, the NCM/MAG cell using LiBOB-1NM3 as the electrolyte demonstrated more than 80% capacity retention at the $C/20$, $C/10$, and $C/5$ rates. However, less than 40% capacity was retained at the $C/2$ rate. The severe capacity fading is attributed to
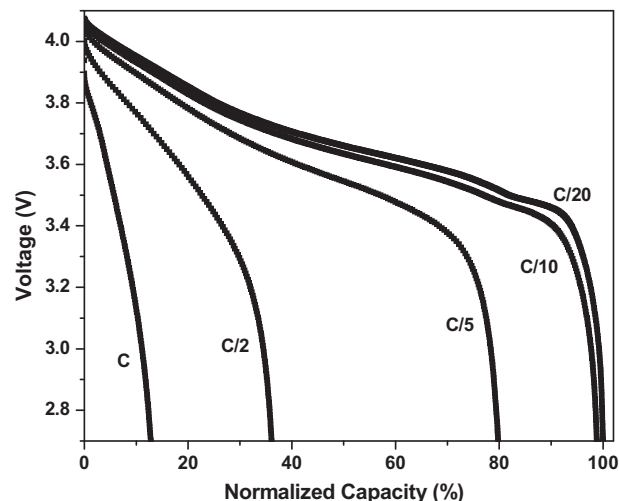
Fig. 7. Discharge profiles of NCM/1NM3-LiBOB/MAG cells at different C-rates with cutoff voltage of 2.7–4.1 V.

the growing SEI formed by the continuous decomposition of LiBOB on the graphite anode surface at higher voltage [19,20,22].

4. Conclusions

The tri(ethylene glycol)-substituted trimethylsilane (1NM3) was synthesized and evaluated as electrolyte solvent with a variety of lithium salts. The ionic conduction behavior of the electrolyte system agrees well with the VTF equation. The ion transport in the electrolyte system is dominated by the mobility of the solvent molecule and the conductivity is correlated with the ion-hopping mechanism. Cycling results showed that the 1NM3-LiBOB exhibits great stability over the other lithium salts due to the SEI formation capability of the LiBOB salt. Additionally, we found that the rather lower ionic conductivity of 1.2 M 1NM3-LiBOB electrolyte is indicative of a much improved cycling performance in an NCM/MAG cell. A possible explanation is that the 1NM3-LiBOB electrolyte with higher concentration would be able to maintain sufficient transport performance even after a significant consumption of the LiBOB salt during the first formation cycle. A critical full cell upper cutoff potential, 4.2 V, was then identified for 1NM3-LiBOB as the electrolyte in NCM/MAG chemistry. Extensive investigations involving the state-of-the-art $LiPF_6$ salt in 1NM3 electrolyte system and the development of novel SEI additives tailored for $1NM3/LiPF_6$ electrolyte system are in progress and will be reported in a separate paper.

Acknowledgements

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