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SHORT COMMUNICATION

Vinyl ethylene carbonate as an additive to ionic liquid electrolyte for lithium ion batteries

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Abstract In this research, we investigated the potential application of vinyl ethylene carbonate (VEC) and ethylene carbonate (EC) as solid electrolyte interface (SEI) film-forming additive in 1-ethyl-3-methylimidazolium (EMI)-bis(trifluoromethyl-sulfonyl) imide (TFSI)-LiTFSI ionic liquid electrolyte (IL). The electrochemical performance of natural graphite (NG7) was studied in LiTFSI/EMI-TFSI containing different weight percent of EC/VEC via cyclic voltammetry (CV), electrochemical impedance spectrum (EIS), and galvanostatic charge/discharge cycles. Temperature effect on the discharge/charge performance of NG7 electrode in the researched IL electrolyte was also discussed.

Keywords Vinyl ethylene carbonate · Solid electrolyte interface · Ionic liquid · Cyclic voltammetry · Additives · Lithium ion batteries

1 Introduction

Lithium ion batteries are widely used as power sources for various electronic devices due to their high energy density and long cycle life. At present, lithium ion batteries have been successfully applied to mobile phone, digital cameras, notebook computers, and personal digital assistance (PDA). For the next generation of lithium ion batteries, they are not only to be used in the electronic devices, but also to be applied to vehicles [1, 2]. Large-scale power lithium ion batteries are necessary to be produced to act as the power sources of vehicles instead of gasoline. Unfortunately, till now large-size power lithium ion batteries are commercially unavailable because of the safety problem [3].

Ionic liquids (ILs), namely room temperature molten salts, have been attracting much attention used as electrolytes in lithium ion batteries by their unique properties such as no measurable vapor pressure, non-flammability, high thermal, and electrochemical stability, high conductivity in wide temperature range [4, 5]. The replacement of flammable organic electrolyte with ILs would greatly improve the safety of lithium ion batteries. 1-ethyl-3-methylimidazolium (EMI) based ILs are commonly used in lithium ion batteries with the combination of anions and lithium salts. However, EMI cations are prone to being reduced at low potential, due to the C–H proton sandwiched between the two nitrogen atoms of the imidazolium cation, which does not result into a stable, functioning solid electrolyte interface (SEI) film [6]. The reduction of EMI cations denies lithium ion inserting into graphite layers to form LiC_6 compounds. Addition of SEI film-forming additives may suppress the reduction of EMI cations and thus allows lithium ion inserting into graphite layers. Till now, ethylene carbonate (EC), vinylene carbonate (VC), chloride EC (Cl-EC), and ethylene sulphite (ES) have been used in ILs as SEI-forming agents to control the reduction of organic cations and showed good performance [7–9].

Vinyl ethylene carbonate (VEC) has been used as SEI film-forming agent in propylene carbonate based liquid electrolyte [3, 10]. In this research, we studied the potential application of VEC as an additive in EMI-bis(trifluoromethyl-sulfonyl) imide (TFSI)-LiTFSI based ionic liquid electrolyte.

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2 Experimental

The preparation of EMI-TFSI-LiTFSI was carried out according to the following procedure. EMI chloride (Acros, 97%) was dissolved in dichloride methane, and then converted into the corresponding TFSI by anion exchange. The obtained EMI-TFSI was vacuum dried at 403 K for 12 h. It was moved into the glove-box filled with Argon gas and mixed with LiTFSI (3 M, 99.95%). The mixture was stirred for several hours and thus homogenous solution of 1.0 mol L^{-1} LiTFSI/EMI-TFSI was obtained. EC (Merck, 99.95%), VEC (Aldrich, 99%) were added to the IL electrolyte with varied ratios. The composition of IL electrolytes was summarized in Table 1.

The half cell was assembled with natural graphite (NG7, Osaka gas) composite electrode as the working electrode, Li metal as the counter and reference electrode. The NG7 composite electrodes were prepared by coating slurries consisting of NG7 (92 wt%) with poly(vinylidene fluoride) (PVDF) (8 wt%) as a binder dissolved in 1-methyl-2-pyrrolidinone (NMP) solution onto copper foil. The NG7 electrodes were dried in vacuum oven at 403 K for 24 h. Celgard 3501 membrane soaked with prepared IL electrolyte was used as the separator. The assembling of half cells was handled in a glove-box filled with dry argon and in which the content of oxygen and moisture is less than 1 ppm.

The electrochemical performance was carried out by cyclic voltammetry (CV) with sweep rate of 0.1 mV s^{-1} between 0 V and 3.0 V (vs. Li/Li^+) using Solartron 1287 Electrochemical Interface. Galvanostatic charge–discharge cycles were performed at 0.1 C rate between 0 V and 3.0 V with Land CT2100A Battery Tester. The electrochemical impedance spectra (EIS) measurements were carried out using Solartron 1260 Gain Phase Analyzer. The frequency range was from 1 MHz to 0.1 Hz. The morphology of the NG7 before and after CV was observed by scanning electron microscope (SEM, Hitachi S300, Philips XL30).

Table 1 The composition of IL electrolytes

IL electrolyte No.	Composition
IL-1	1.0 mol L^{-1} LiTFSI-EMI-TFSI
IL-2	1.0 mol L^{-1} LiTFSI-EMI-TFSI + 5 wt%EC
IL-3	1.0 mol L^{-1} LiTFSI-EMI-TFSI + 10 wt%EC
IL-4	1.0 mol L^{-1} LiTFSI-EMI-TFSI + 5 wt%VEC
IL-5	1.0 mol L^{-1} LiTFSI-EMI-TFSI + 10 wt%VEC
IL-6	1.0 mol L^{-1} LiTFSI-EMI-TFSI + 15 wt%VEC
IL-7	1.0 mol L^{-1} LiTFSI-EMI-TFSI + 5 wt%EC/ 5 wt%VEC

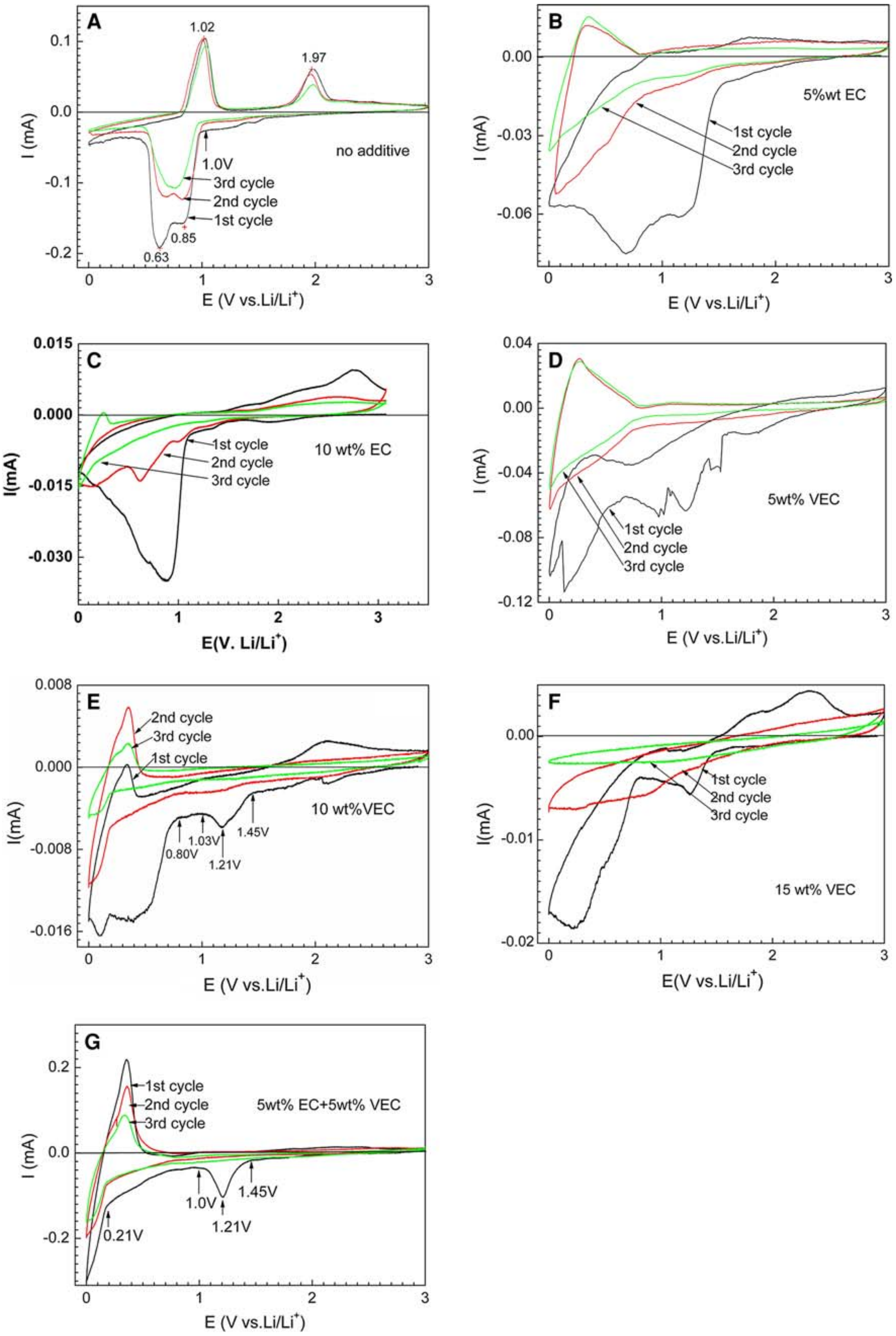
Fig. 1 Cyclic voltammograms of NG7 electrode in 1.0 mol/L▶ LiTFSI/EMI-TFSI IL electrolytes containing different percent of additives (**a** no-additive, **b** 5 wt% EC, **c** 10 wt% EC, **d** 5 wt% VEC, **e** 10 wt% VEC, **f** 15 wt% VEC, **g** 5 wt%EC + 5 wt%VEC. Scan rate: 0.1 mV s^{-1}.)

3 Results and discussion

3.1 The electrochemical performances of researched system

The electrochemical performances of researched IL electrolytes were measured by CV and charge–discharge cycles. Figure 1 shows the CV cycles of NG7/Li half cells with 1.0 mol L^{-1} LiTFSI/EMI-TFSI containing different weight percent of additives. When NG7 electrode was cycled in IL-1 electrolyte (additive free), in the first cathodic process, two current peaks can be observed in the potential range between 1.0 V and 0.4 V (vs. Li/Li^+) and two corresponding anodic peaks appeared in the following anodic process between 0.7 V and 2.2 V, just as shown in Fig. 1a. The cathodic and anodic current peaks should be attributed to the reduction of EMI cations and intercalation/de-intercalation of EMI cations into/from graphite layers [9, 11, 12]. Because of the reduction of EMI cations, SEI film cannot be formed on the surface of graphite and thus suppress lithium ion inserting into graphite layers. From above result, we knew that LiTFSI/EMI-TFSI can not be used as an electrolyte in lithium ion batteries due to the EMI reduction and intercalation prior to lithium ion insertion. Film-forming additives are necessary to be applied to IL electrolytes to form SEI film on the surface of graphite electrode before EMI cations reduction and intercalation occured.

EC, the common film-forming agent, was added to LiTFSI/EMI-TFSI and the contents of EC is 5 wt% and 10 wt%. The NG7 electrodes were cycled in the prepared IL electrolyte. As shown in Fig. 1b and c, the addition of EC changed the electrochemical behavior of EMI cations. In the cathodic sweep, the reduction of EMI cations still took place, but the values of peak current are much smaller than that of IL-1 and no obvious current peak can be observed in the following anodic sweep. This is a typical phenomenon that the graphite materials exfoliated. In the second and third cycles, lithium ion inserted into the electrode in the cathodic process and extracted from it in the following anodic process, but we found that lithium ion insertion started from about 1.0 V and did not show stage phenomenon. It represents the electrochemical behavior of disorder carbon. The above result indicated that the addition of EC can not suppress the reduction and intercalation of EMI and thus the natural graphite electrode exfoliated after the reduction and intercalation of EMI cations.


A
1.02
1.97
no additive
1.0V
3rd cycle
2nd cycle
1st cycle
0.85
0.63
I (mA)
E (V vs.Li/Li+)
B
5%wt EC
1st cycle
2nd cycle
3rd cycle
I (mA)
E (V vs.Li/Li+)
C
10 wt% EC
1st cycle
2nd cycle
3rd cycle
I(mA)
E(V. Li/Li+)
D
5wt% VEC
1st cycle
2nd cycle
3rd cycle
I (mA)
E (V vs.Li/Li+)
E
2nd cycle
3rd cycle
1st cycle
10 wt%VEC
0.80V
1.03V
1.21V
1.45V
I(mA)
E (V vs.Li/Li+)
F
1st cycle
2nd cycle
3rd cycle
15 wt% VEC
I(mA)
E(V vs.Li/Li+)
G
1st cycle
2nd cycle
3rd cycle
5wt% EC+5wt% VEC
0.21V
1.0V
1.21V
1.45V
I (mA)
E (V vs.Li/Li+)

Then, VEC was add into LiTFSI/EMI-TFSI as SEI film-forming additive with different contents. The cyclic voltammograms of test cells are shown in Fig. 1d, e and f. We observed a new cathodic peak at ca. 1.21 V in the first cathodic sweep, which corresponds to the SEI film formation originating from the reduction of VEC [3]. The addition of VEC improved the interfacial compatibility between NG7 electrode and IL electrolyte. With the addition of VEC the reduction and intercalation of EMI cations were suppressed more or less, especially in the case that the content of VEC is 10 wt%. From Fig. 1e, we observed that the starting potential of EMI reduction delayed from 1.0 V to 0.8 V and the cathodic/anodic peaks corresponding to lithium ion insertion/extraction into/from graphite structures appeared in the first cycle. In the later CV cycles, cathodic peaks characteristic of EMI reduction was not observed any more and lithium ion inserted into and extracted from graphite layers reversibly, but the peak current faded rapidly. The result manifested that VEC can be used in LiTFSI/EMI-TFSI as SEI-forming additive to suppress the EMI reduction and intercalation, but the formed SEI film is not stable and it cannot fully protect the electrolyte from further reduction at low potential, which led to the bad cyclic ability of tested cell.

From above results and discussion, we learned that sole EC or VEC is not a satisfactory SEI-forming additive to be used in LiTFSI/EMI-TFSI IL electrolyte. Thinking of the difference of reduction potential ranges for EC and VEC, we mixed EC and VEC equally as co-additive to the researched IL electrolyte and the contents of EC and VEC is 5 wt% and 5 wt%, respectively. The electrochemical performance of NG7 electrode in IL electrolyte containing 5 wt%EC/5 wt%VEC is shown in Fig. 1g. In the first cycle, a cathodic peak at 1.21 V corresponding to reduction of VEC was observed and it was no longer appeared in the second and third cycles. And from 1.0 V the cathodic current increased slowly till 0.21 V, which corresponds to the reduction of EC to form SEI film on the surface of NG7 electrode. From 0.21 V the cathodic current increased rapidly and reached the peak at ca. 0 V, which is characteristic of lithium ion insertion into graphite layers. In the anodic sweep, extraction of lithium ion can also be observed at ca. 0.22 V. In the later CV cycles, the insertion and extraction of lithium ion shows good cyclic ability. From CV cycles, we concluded that a stable SEI film formed on the surface of NG7 electrode with the addition of 5 wt% EC/5 wt% VEC co-additive in IL electrolyte. The formation of a compact, insoluble SEI film can protect the electrolyte from further reaction at low potential. Therefore, the reduction and intercalation of EMI cations were suppressed. Moreover, the peak current intensity of lithium ion insertion/extraction in ILs containing 5 wt% EC/5 wt% VEC (IL-7) is one order more than that of ILs containing 10 wt% VEC (IL-5). It indicated that the resistance of lithium ion insertion/extraction into/from graphite structure is much smaller in IL-7 than that in IL-5, which was confirmed in EIS (see Fig. 2).

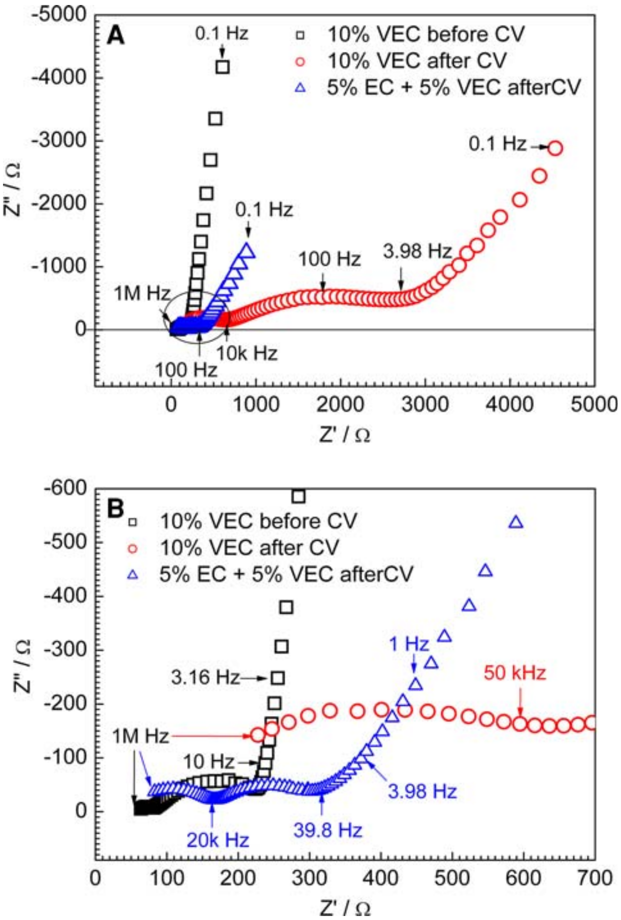


Fig. 2 Niquist plots of NG7 electrode CV cycled in 1.0 mol L^{-1} LiTFSI/EMI-TFSI with 10 wt%VEC and 5 wt% VEC + 5 wt% EC. (**a** The whole spectrum; **b** The enlarged spectrum of (**a**))

EIS measurements were carried out after three CV cycles to ensure the SEI film was fully developed. In EIS the high-to-medium frequency semicircle is commonly attributed to the SEI film formed on the surface of graphite. From Fig. 2, it was found that a depressed semicircle appeared in the high-to-medium frequency region for IL-7 and in the counterpart region a very large spur existed for IL-5. Comparison of EIS between two samples shows that the SEI film resistance of the cell using IL-5 electrolyte is much larger than that obtained in IL-7 electrolyte. The difference of SEI film resistance led to the difference of current peak intensity.

From CV cycles and EIS, we drew a conclusion that the EC/VEC co-additive has a good ability to form stable SEI film on the surface of NG7 electrode in LiTFSI/EMI-TFSI. The reduction and intercalation of EMI cations can be suppressed in this system and lithium ion can insert/extract into/from graphite layers reversibly.

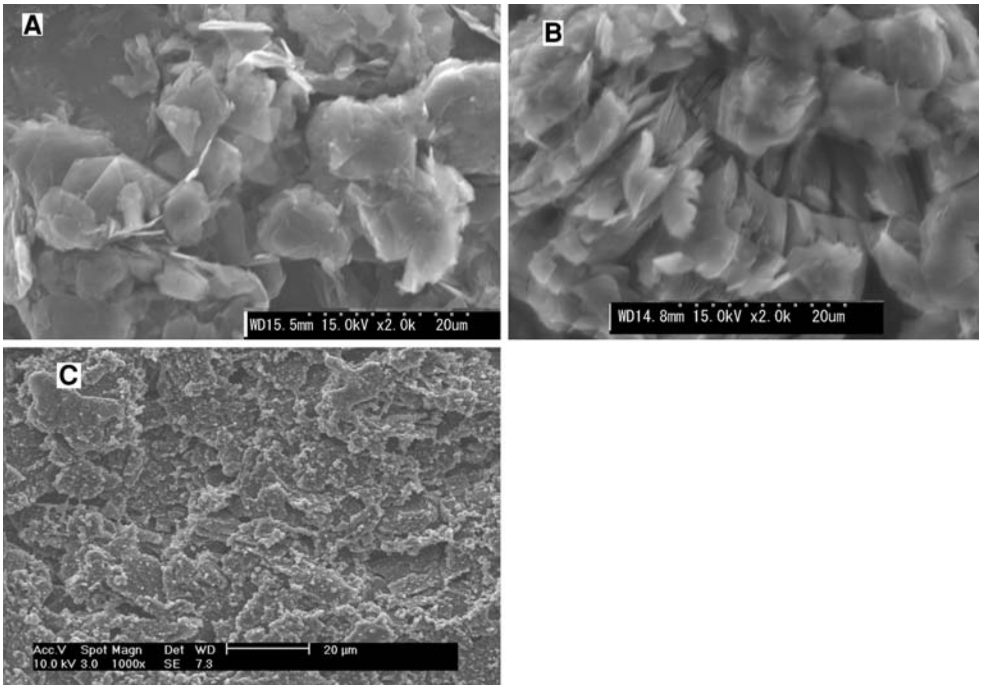


Fig. 3 SEM images of NG7 electrodes: **a** Pristine electrode, **b** Electrode cycled in IL-3, **c** Electrode cycles in IL-7

3.2 The mechanism related to SEI film formation of EC/VEC co-additive

EC/VEC co-additive shows good ability to form SEI film on the surface of graphite in LiTFSI/EMI-TFSI, which should be attributed to cooperation of EC and VEC. The potential corresponding to reduction of VEC is in the range from 1.45 V to 1.0 V and the potential for reduction of EC began at ca. 1.0 V and ended at the potential before lithium ion insertion, i.e., from 1.45 V till lithium ion insertion, SEI film formed successively. The potential for EMI reduction located in the range of VEC reduction potential and is higher than that of EC reduction. Therefore, for sole VEC additive a stable SEI film has not yet formed and for sole EC additive SEI film just begins to grow when EMI cations are reduced on graphite surface. With joint use of VEC and EC SEI film grew continuously. The SEI film formation from VEC just finished, and the reduction of EC started and new SEI film formed on the base of reductive products of VEC. In this process, a stable and compact SEI film grew gradually. EMI cation, due to its large volume, cannot go through this film. Therefore, the reduction and intercalation of EMI is suppressed and graphite kept its original structure, which guaranteed that lithium ion inserted into and extracted from graphite structures reversibly.

After experiencing different SEI film formation process, NG7 electrode showed different morphology, as shown in Fig. 3. The pristine NG7 materials are in the shape of flake (see Fig. 3a). For the NG7 electrode after CV cycles in 1.0 mol L^{-1} LiTFSI/EMI-TFSI containing 10 wt% VEC, exfoliation of graphite structure was clearly observed in the SEM image as shown in Fig. 3b. Figure 3c is the image of NG7 electrode after CV cycles in 1.0 mol L^{-1} LiTFSI/EMI-TFSI containing VEC/EC (5 wt%/5 wt%). From Fig. 3c, we observed that the surface of NG7 electrode was coated with some substances and we did not find graphite exfoliated in the image. The coating on the surface of graphite should be related with SEI film.

3.3 Temperature effect on the charge and discharge cycles of NG7 in IL electrolyte containing EC/VEC additives

LiTFSI/EMI-TFSI electrolyte containing 5 wt% EC/5 wt% VEC shows good compatibility with NG7 electrode. We also evaluated the cycle performance of assembled cells by discharge–charge measurement at 0.1 C at room temperature, just as shown in Fig. 4a. Unfortunately, the discharge specific capacity in the first cycle is 220 mAh g^{-1}, which is much lower than the theoretic specific capacity of graphite, 372 mAh g^{-1}. The specific capacity decreased rapidly with cycles and in 30th cycle the discharge capacity remained ca. 20 mAh g^{-1}. The discharge and charge cycle performance of NG7 electrode in researched IL electrolyte is very poor.

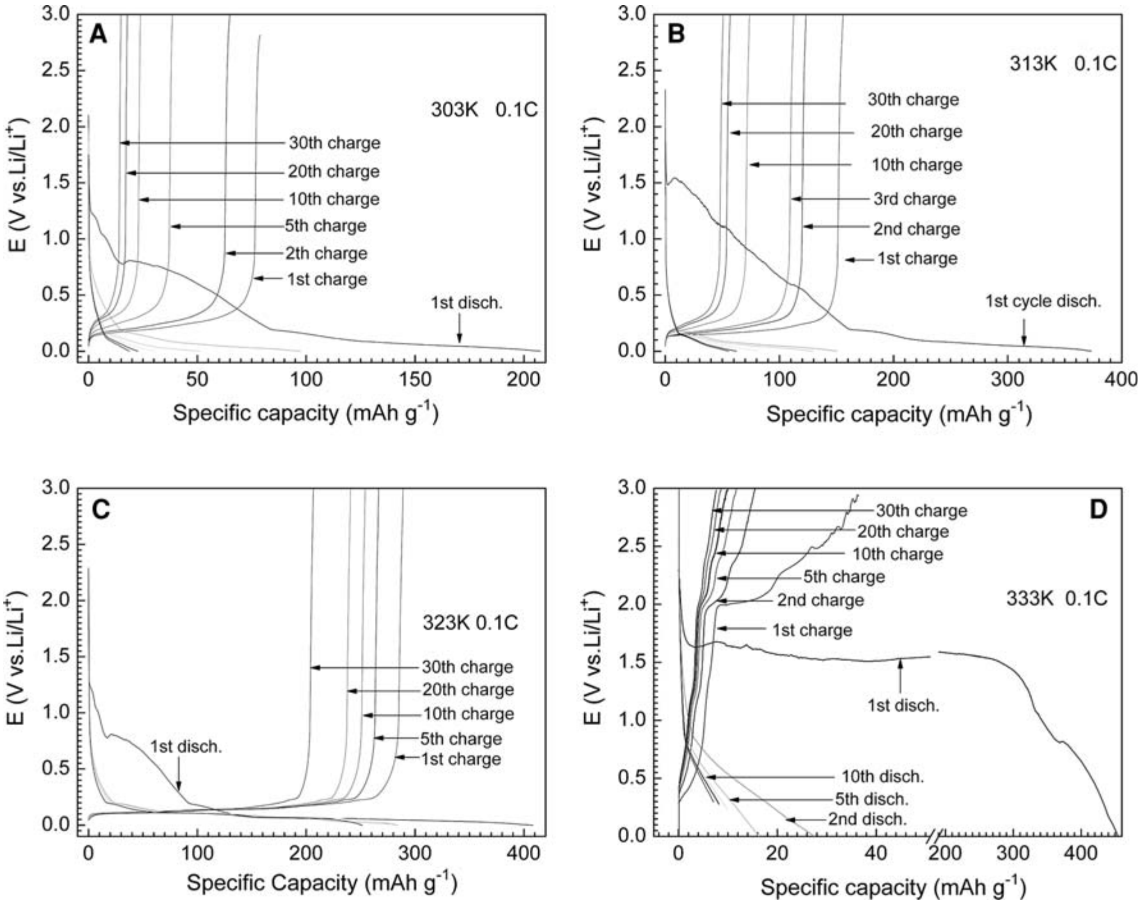


Fig. 4 The voltage profiles of NG7/Li half cells with IL-7 electrolyte at different temperatures: **a** 303 K, **b** 313 K, **c** 323 K, **d** 333 K

In view of low ionic conductivity for most of IL electrolyte at room temperature [13], we considered that the low specific capacity and poor cycle performance is attributed to low ionic conductivity which led to high polarization. Therefore, the temperature has an effect on the discharge–charge cycle performance. We investigated the discharge–charge behavior of NG7 electrode in 1.0 mol L^{-1} LiTFSI/EMI-TFSI containing 5 wt% EC/5 wt% VEC under the temperature of 303 K, 313 K, 323 K, and 333 K, respectively (see Fig. 4). From Fig. 4 it can be observed that at first the specific capacity of discharge and charge increased with temperature rising, and at 323 K the reversible capacity in the first cycle reached to 290 mAh $g^{-1}$and after 30 cycles it remained 205 mAh g^{-1}. It showed the best discharge and charge performance in the set temperatures. However, when the temperature rises to 333 K the electrochemical performance deteriorated and the tested cell could not be charged and discharged at all.

The improvement of discharge and charge performance from 303 K to 323 K should be attributed to the weakening of polarization because the ionic conductivity of ILs electrolyte increased with the temperature rising. The deterioration of discharge and charge at 333 K may be ascribed to the instability of SEI film in high temperature [14].

4 Conclusion

EC/VEC co-additives can improve the interfacial compatibility between NG7 electrode and LiTFSI/EMI-TFSI IL electrolyte. With the addition of 5 wt% EC/5 wt% VEC in 1.0 mol L^{-1} LiTFSI/EMI-TFSI, a stable SEI film formed on the surface of NG7 electrode, the reduction and intercalation of EMI cations were suppressed and lithium ion inserted/extracted into/from the graphite layers reversibly. The improvement on electrochemical performance of tested system is attributed to the cooperation of EC and VEC because the SEI formation of EC/VEC is a continuous process in the potential range from 1.45 V till lithium ion inserting into graphite structure.

Temperature has an effect on the charge/discharge performance of NG7 electrode in LiTFSI/EMI-TFSI IL electrolyte containing EC/VEC co-additives. At room temperature, the cyclic ability of researched half cell is poor, which is related with polarization caused by low ionic conductivity of IL electrolyte. From room temperature to 323 K, the specific capacity of discharge/charge increased with temperature rising.

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