In-situ Optical Microscope Morphology Observation of Lithium Electrodeposited in Room Temperature Ionic Liquids Containing Aliphatic Quaternary Ammonium Cation

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Abstract

The behavior of lithium (Li) electrodeposition in room temperature ionic liquids (RTILs) containing aliphatic quaternary ammonium cation was investigated by in-situ optical microscope observation. As a result, round shape Li deposits were obtained after deposition in all cases with vinylene carbonate (VC) as an additive, while most deposits were dendritic without VC. AC impedance spectroscopic measurements indicated that the dendrite growth was suppressed when a surface film with large resistance was generated. The dendrite suppression effect by VC addition was confirmed in the Py14[TFSA]-based and TMHA[TFSA]-based electrolytes as well as in the PP13[TFSA]-based electrolyte.

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1. Introduction

Li metal is a candidate for negative electrode materials with larger capacity density than carbonaceous materials, meaning that Li metal battery systems are expected to show higher energy density. From this view continuous research is underway to utilize the Li anode for rechargeable batteries, although it is not yet widespread.1 One of the biggest obstacles to its commercialization is Li dendritic growth on the negative electrode during charging, which causes short circuits and poor cycleability.2 Aurbach’s group proposed one mechanism for the Li dendrite formation.3–5 First, the electrolyte, usually organic electrolyte, reacts with Li metal, generating surface film. When Li is deposited, the volume of Li metal of the electrode is increased and a part of the surface film cracks. Li ion easily passes through the crack and Li deposition concentrates in the crack. Dendritic lithium can cause short circuits by penetrating the separator, which affects the safety. During discharging, dendritic lithium can also form Li isolated from the electrolyte, so-called “dead lithium”, which leads to poor cycleability. So the property of the surface film is thought to be a significant parameter affecting the morphology of the electrodeposited Li, and therefore the safety and the cycleability.

It is very important to investigate the conditions for dendrite-free Li electrodeposition. There are many studies on the electrodeposited Li morphology in apotic organic solvents,1,2,6,7 but few in room temperature ionic liquids (RTILs).8–12 Among RTILs, we are interested in those which are stable at cathodic conditions such as Li redox potential,2,9,13,14 because they might form either no surface film or a different type of surface film from those formed in the case with conventional organic electrolyte. We recently reported on the morphology of electrodeposited Li.9,10 In PP13[TFSA]-based (PP13; N-methyl-N-propylpiperidinium, TFSA; bis(trifluoromethyl-sulfonyl)amide) electrolyte with 3 wt% addition of VC, fine non-dendritic particles were obtained, while dendritic Li was obtained without VC. In this case, VC addition had an effect of dendrite suppression. This effect was also confirmed in PP13[TFSA]-based (FSA; bis(fluorosulfonyl)amide) electrolyte, although some deposits were still dendritic in PP13[FSA]-based electrolyte with VC. This effect was not seen when using EMIM[TFSA]-based (EMI; 1-ethyl-3-methylimidazolium) and EMIM[TFSA]-based electrolytes. The common features with the RTIL in the electrolyte of which VC had a dendrite suppression effect were (i) high viscosity, (ii) stable at cathodic condition such as Li redox potential, and (iii) PP13-cation-containing. In this study, to discuss further and better understand the main factors in dendrite suppression, the Li electrodeposition behaviors in electrolytes of other RTILs were investigated. Py14[TFSA] (Py14; N-methyl-N-butylpyrrolidinium) and TMHA[TFSA] (TMHA; trimethyl-hexylammonium) were selected according to the strategy as follows: (i) Carbon numbers of cations are the same as that of PP13 cation. (ii) Cathodic stability is as high as PP13[TFSA]. (iii) Viscosity of the RTILs varies from 70 to 150 cP. In-situ optical microscope observation, without surface state changes or morphology changes by sampling processes involving rinsing and transportation, was used to examine the morphology of the Li deposits.

2. Experimental

Electrolyte preparation was carried out in a dry room in accordance with the previous reports.13,15 0.32 mol kg⁻¹ (ca. 10 wt%) of Li[TFSA] (Kishida Chemical) was added to PP13[TFSA] (Kanto Chemical, 150 mPas), Py14[TFSA] (Kanto Chemical, 71.5 mPas), and TMHA[TFSA] (Kishida Chemical, 153 mPas) (Fig. 1). 0.35 mol kg⁻¹ (ca. 3 wt%) of VC was added to each electrolyte.

Cell fabrication was carried out in an Argon (Ar)-filled glove box in accordance with the previous reports.2 For the in-situ optical microscope observation, a custom-made two-electrode cell was fabricated. The working electrode was nickel (Ni) foil (Nilaco, 99.7%) and the counter electrode was Li thin film pasted on copper foil (Honjo metal). The distance between the two electrodes was 1 mm by a spacer ring. The working electrode surface was observed in-situ by an optical microscope through a hole on the counter electrode and a quartz glass window in the cell. The lithium electrodeposition was carried out with 50 µA cm⁻² of current density.
for 60,000 s, corresponding to a total charge amount of 3 C cm\(^{-2}\). Before opening the cells, the potentiostatic ac impedance spectra at open circuit potential was measured with the two-electrode method, using an ac amplitude of 10 mV and frequency range of 10\(^5\) to 1 Hz.

The cathodic stability of each RTIL without Li salt was examined by linear sweep voltammetry in an Ar-filled glove box. A Ni electrode with surface area of 0.196 cm\(^2\) was used as the working electrode and a platinum (Pt) wire was used as the counter electrode. The I\(^3\)/I\(^1\) reference electrode for the RTILs, which consisted of a Pt wire/0.015 mol dm\(^{-3}\) I\(_2\) + 0.060 mol dm\(^{-3}\) [(n-C\(_3\)H\(_7\))\(_4\)N]I in EMI[TFSI], was used. The potential was referenced to the ferrocene (Fc)/ferrocenium (Fc\(^+\)) redox couple in each RTIL.

3. Results and Discussion

The voltage-time profiles for the cell with Py14[TFSA]-based electrolyte and with VC are shown in Fig. 2 and the in-situ optical microscope images of the Li-deposited Ni electrode are shown in Fig. 3 for the case without and with VC. Only the initial 1,400 s of the deposition time is shown in Fig. 3, although the total deposition time was 60,000 s. In both cases, side reactions were observed when the voltage reached 1.5 V, and this side reaction proceeded until the voltage reached 0 V in about 800 s. Just after the cell voltage reached 0 V, the lithium deposits were observed (Fig. 3), which means that nuclei of Li deposits were generated at that time. VC addition did not have an effect on the time taken for the nuclear generation, which indicates that the charge used for reduction of VC was not so large. After 60,000 seconds, dendritic Li was observed without VC. In contrast, with VC, round-shape Li was observed (Figs. 4(a) and 4(b)) which means that nuclei of Li deposits were generated at that time. VC addition did not have an effect on the time taken for the nuclear generation, which indicates that the charge used for reduction of VC was not so large. After 60,000 seconds, dendritic Li was observed without VC. In contrast, with VC, round-shape Li was observed (Figs. 4(a) and 4(b)). The same tendencies of voltage change and morphology were confirmed also for the cell with PP13[TFSA]-based electrolyte\(^e\) and for the cell with TMHA[TFSA]-based electrolyte [Figs. 4(c) and 4(d)]. The dependency of the current density on the deposition morphology is not studied in this study, because PP13[TFSA]-based and TMHA[TFSA]-based electrolytes are too viscous to increase the current density.

Figure 5 shows the ac impedance spectra as Nyquist plots for the cells with PP13[TFSA]-based, Py14[TFSA]-based, and TMHA[TFSA]-based electrolytes. One or two depressed semicircles were observed in the lower frequency region and a line or a part of a small semicircle was observed in the higher frequency region, similar to the report by Aurbach and Zaban.\(^{17}\) They proposed that the structure of the interface between Li and electrolyte can be modeled as a combination of an R component of solution resistance and RC components which come from some interfaces and bulk.
cathodic limit potential was de-

thought to be as stable against reduction as PP13\[TFSA\]. Here the

VC would form a

mechanism for the dendrite suppression: The combination of a RTIL

TMHA\[TFSA\] is ca.

indicate that the cathodic limit potential of Py14\[TFSA\] and

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linear sweep voltammograms in the negative scans shown in Fig.6

cases with and without VC,9,10 and in that report, we proposed a

the difference in the morphology of electrodeposited Li between the

surface but also on the working electrode surface.

impedance spectra contain information about both the working
electrode surface and the counter electrode surface, it is thought that
the resistance increase was caused not only on the counter electrode
surface but also on the working electrode surface.

For the PP13\[TFSA\]-based electrolyte, we have already reported

that the same mechanism applies in the case with Py14\[TFSA]-

based electrolyte and TMHA\[TFSA]-based electrolyte with VC, since the same combination of a RTIL with cathodic stability and VC was used.

The viscosities of PP13\[TFSA\] and TMHA\[TFSA\] are similar, while that of Py14\[TFSA\] is half those of the others (see Experimental). In systems with low viscosity, high mobility of Li ion can be expected, increasing the Li ion supply concentration to rather active sites, and thus, dendritic growth of Li. But in fact there were no differences in the dendrite suppression effect between the three systems with VC, so the viscosity did not have a large effect on the dendrite suppression in these cases. The result obtained in this study indicates that the morphology of the electrodeposited Li would be affected more by the stability of the RTIL for reduction than by the viscosity of the RTIL.

4. Conclusion

We compared the behavior of lithium electrodeposition in

PP13\[TFSA\]-based, Py14\[TFSA\]-based, and TMHA\[TFSA\]-based electrolytes with and without VC as an additive, where each of the base RTILs contains an aliphatic quaternary ammonium cation. By in-situ optical microscope observation and ac impedance spec-
troscopy, a dendrite suppression effect was newly confirmed for the cells with Py14\[TFSA\]-based and TMHA\[TFSA\]-based electrolytes containing VC as well as PP13\[TFSA\]-based electrolyte containing VC. At that time, a surface film with high resistance which was thought to mainly consist of VC-originated components was formed. The morphology of the Li deposit was affected more by the cathodic stability than by the viscosity of the electrolyte base among the electrolytes used in this study.

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References