Short communication

Application of electrolyte using novel ionic liquid to Si thick film anode of Li-ion battery

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ABSTRACT

An applicability of a novel ionic liquid, consisting of 1-methoxyethoxymethyl(tri-*n*-butyl)phosphonium cation and bis(trifluoromethanesulfonyl)amide anion, was investigated as an electrolyte of Li-ion battery using a thick film electrode of Si prepared by a gas-deposition method. The electrochemical properties in the novel ionic liquid were compared to those in a commercial ionic liquid and a typical organic solvent of propylene carbonate. The initial discharge capacity of 3450 mAh g^{-1} and excellent cycling performance were achieved in the novel ionic liquid. The novel ionic liquid was confirmed to effectively suppress a collapse and an electrical isolation of the Si thick film induced by pulverization during charge–discharge cycling. The excellent performance is possibly attributed to more effective desolvation of Li ions from the anions due to its lower dielectric constant compared with the propylene carbonate solvent.

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1. Introduction

Silicon anode materials have attracted much attention as alternative to a graphite anode in a commercial Li-ion battery because its theoretical capacity of 4200 mAh g^{-1} is much larger than that of graphite (372 mAh g^{-1}). The huge capacity is extremely attractive as a next-generation anode, and is originated from an alloying reaction of Li–Si up to a composition ratio of Li$_{4.4}$Si [1–3]. However, Si anode has some disadvantages of a high electrical resistivity, a low diffusion coefficient of Li ion in Si [4], and a drastic change of specific volume during the alloying/dealloying reactions. The Li$_{22}$Si$_5$ (Li$_{4.4}$Si) has a cubic crystal structure with a lattice constant of 1.875 nm [5]. The unit cell volume is approximately 6.592 nm^3. However, there are 80 Si atoms in the unit cell of Li$_{22}$Si$_5$ [5]. Thus, the volume per Si atom corresponds to be 0.0824 nm^3. On the other hand, cubic Si has a lattice constant of 0.5431 nm and the unit cell volume of 0.160 nm^3. The volume per Si atom is 0.020 nm^3 because the Si unit cell includes eight Si atoms. Therefore, in the structure change from Si to Li$_{4.4}$Si, the volumetric change ratio per Si atom corresponds to be 410%. The drastic volumetric change causes a breakup of the electrode and an electrical isolation of the active material of Si. Consequently, the electrode performance of Si anode rapidly fades away by repeating Li-insertion and extraction. When

a silicide instead of elemental Si is utilized as the active material of anode, the capacity is drastically lost owing to smaller storage amount of Li ions in the silicide. Therefore, we believe that anodes for the next-generation Li-ion battery should mainly consist of elemental Si to derive an advantage of its larger theoretical capacity.

A gas-deposition (GD) method is a suitable technique to form thick films. In this method, an aerosol consisting of raw particles and a carrier gas gushes from a nozzle to a substrate with a high speed in the range of the sonic speed. For preparing electrodes, we have demonstrated that the GD method gives various advantages including (i) the strong adhesion between the active material particles as well as between the particles and the substrate, (ii) the nearly unchanged composition in thick film formed without atomization (e.g., vaporization) of the particles such as vaporization, and (iii) the formation of interstitial spaces between the particles, which is a favorable structure to release the stress induced by the volumetric change of the active material particles [6,7]. By using the gas-deposition of Si-based materials, we have prepared GD-film electrodes with both a large capacity and better cycling performance [8–11].

An electrolyte is also one of the most important components in Li-ion battery. Typical electrolytes in commercialized Li-ion batteries consist of an organic solvent based on ethylene carbonate ($C_3H_4O_3$; EC) and a lithium salt such as lithium hexafluorophosphate (LiPF$_6$). The EC-based electrolytes have brought out a favorable electrode performance and an excellent stability. However, the electrolytes have been optimized for a graphite
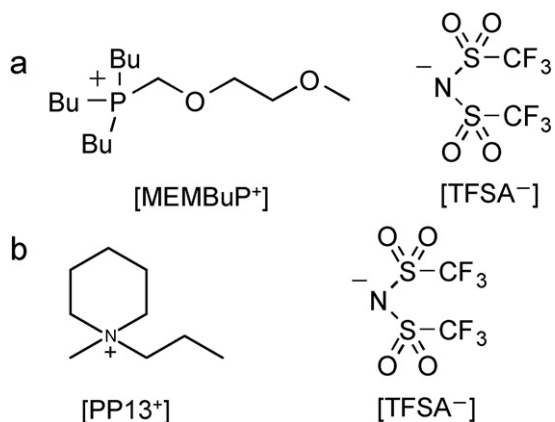
Fig. 1. Molecular structure of ionic liquids used in this study. (a) 1-Methoxyethoxymethyl(tri-*n*-butyl)phosphonium bis(trifluoromethanesulfonyl)-amide, [MEMBu₃P⁺][TFSA⁻], synthesized by Itoh et al. [20] and (b) a commercial ionic liquid of 1-methyl-1-propylpiperidinium bis(trifluoromethanesulfonyl)-amide, [PP13⁺][TFSA⁻].

anode in existing Li-ion batteries. It is necessary to develop new electrolyte suitable for a next-generation anode using Si-based materials because a mechanism of Li-storage in the Si-based anode is the alloying/dealloying reactions of Li–Si, which is essentially different from a mechanism of intercalation/de-intercalation of Li ions in the graphite anode. Ionic liquids have recently received grovel attentions as a safer electrolyte with higher thermal stability, wider potential window, and lower vapor pressure. Due to these excellent properties, many researchers have studied application of ionic liquids to an electrolyte in Li-ion battery of existing graphite-based anodes [12–15]. On the other hand, there is no study on Si-based anodes obtained by GD method in ionic liquids though some researchers have applied ionic liquids to Si-based anodes prepared by sputtering [16] and slurry [17] methods. Therefore, we are developing a novel ionic liquid which is applicable electrolyte to our GD-film electrodes of Si-based materials.

We have recently synthesized novel ionic liquids containing quaternary phosphonium cations by an organic synthetic method [18–20]. In this study, we investigated an applicability of the novel ionic liquid as an electrolyte of Li-ion battery using Si thick-film electrode prepared by the gas-deposition comparing with a commercial ionic liquid.

2. Experimental

For gas-deposition, Cu foil substrates with the thickness of 20 μm were set up in a vacuum chamber with a guide tube. An aerosol consisting of an Ar gas (differential pressure 7×10^5 Pa) and active material of a commercial Si powder was generated in the guide tube, and gushed from a nozzle with a diameter of 0.8 mm to the Cu substrate in the chamber with a base pressure of 8 Pa. The particle size of the Si powder (Wako Pure Chemical Industries, Ltd., 99%) mainly ranges from 0.2 to 2 μm. Further detailed conditions of the gas-deposition have been described in our previous papers [6,7]. The weight of deposited Si on the substrate was 30–60 μg. The film thickness of the active material was roughly estimated to be 3–6 μm by a cross-sectional observation using a scanning electron microscope (SEM, JSM-5200; JEOL Ltd.).

Two kinds of ionic liquids were used as electrolytes in this study. The molecular structures are compared in Fig. 1. One is 1-methoxyethoxymethyl(tri-*n*-butyl)phosphonium bis(trifluoro-methanesulfonyl)amide [MEMBu₃P⁺][TFSA⁻], a novel ionic liquid containing quaternary phosphonium cation synthesized by our group [20]. The other is 1-methyl-1-propylpiperidinium

bis(trifluoromethanesulfonyl)amide [PP13⁺][TFSA⁻], a commercial ionic liquid (Kanto Chemical Co., Inc.). The anodic decomposition potentials of [MEMBu₃P⁺][TFSA⁻] and [PP13⁺][TFSA⁻] were determined to be 5.1 and 5.5 V vs. Li/Li⁺ by a linear sweep voltammetry with a sweep rate of 0.1 mV s⁻¹ as our preliminary experiment. Electrolytes were prepared by dissolving a salt of lithium bis(trifluoromethylsulfonyl)amide (LiTFSA, Kishida Chemical Co., Ltd.) in these ionic liquids with a concentration of 1.0 mol L⁻¹ (M). For comparison, we used an electrolyte of 1.0 M LiClO₄-dissolved propylene carbonate (PC; $C_4H_6O_3$, Kishida Chemical Co., Ltd.) as an existing electrolyte based on organic solvent.

A two-electrode coin-type cell with 2032 size was assembled in a glove box filled with Ar gas. Working and counter electrodes were the GD-film of Si and a Li sheet with a thickness of 1.0 mm (Rare Metallic, 99.90%). The areas of the Si film and the Li sheet in the cell are 0.28 cm² and 4.90 cm², respectively. A polypropylene film was soaked in the electrolytes and was used as a separator.

Electrochemical measurements were carried out at 303 K using an electrochemical measurement system (HZ-3000 Hokuto Denko Co., Ltd.). Constant current charge–discharge tests were performed under a constant current of 0.42 A g⁻¹, corresponding to a current rate of 0.1 C, and cutoff potentials of 0.005 V vs. Li/Li⁺ for charge (Li-insertion) and 2.000 V vs. Li/Li⁺ for discharge (Li-extraction). In addition, a rate performance of the cell was also examined using a higher current density of 1.0 A g⁻¹ (0.25 C). The surface morphology was observed using a scanning electron microscope (SEM, JSM-5200; JEOL Ltd.) for the electrodes before and after the charge–discharge cycling. Electrochemical impedance spectroscopic (EIS) analysis was conducted at the potential of 0.005 V vs. Li/Li⁺ as the firstly Li-inserted state. The potential amplitude was set to be 10 mV, and the scanned frequency was ranged from 20 kHz to 10 mHz. In the solutions of LiClO₄/PC and ionic liquids without LiTFSA, the conductivity was determined by the EIS analysis in T-type cell with two Pt electrodes. The viscosity of [MEMBu₃P⁺][TFSA⁻] was measured with Brookfield cone and a plate viscometer.

3. Results

The viscosity and conductivity of the electrolytes used in this study are summarized in Table 1. The physical data of [PP13⁺][TFSA⁻] and PC were cited from [21] and [22]. The ionic liquids exhibited very higher viscosities compared with 1 M LiClO₄/PC electrolyte. The higher viscosities are attributed to a coulombic interaction between dissociated cations and anions. There is no significant difference in the viscosity and conductivity between two kinds of ionic liquids, [MEMBu₃P⁺][TFSA⁻] and [PP13⁺][TFSA⁻]. The conductivity of the LiClO₄/PC electrolyte is higher in comparison with both the ionic liquids. It is suggested that the higher conductivity of the LiClO₄/PC electrolyte is caused by its lower viscosity.

Fig. 2 depicts charge–discharge curves of Si thick-film electrodes at the first cycle in the ionic liquids and PC under the current density of 0.1 C. In this study, the charge/discharge means insertion/extraction of Li ions. In every case, potential plateaus appeared at approximately 0.1 and 0.4 V vs. Li/Li⁺ in the charge and discharge reactions. The potential plateaus are originated from alloying and de-alloying reactions of Si with Li. The potential difference between the charge and discharge plateaus is attributed to a polarization of the cell. At the first cycle, the Si electrodes in PC and the ionic liquid containing [MEMBu₃P⁺] cation exhibited large discharge capacities of 3390 and 3450 mAh g⁻¹. The first discharge capacity of 3450 mAh g⁻¹ in the ionic liquid containing [MEMBu₃P⁺] cation was much larger than that of 1900 mAh g⁻¹ in the ionic liquid containing [PP13⁺] cation.

Table 1

Physical properties of solvents and electrochemical performance for Si GD-film electrodes in various electrolytes of ionic liquids and LiClO$_4$/PC. The physical data of [PP13$^+$][TFSA$^-$] and PC were cited from Refs. [21] and [22].

Electrolyte	Viscosity (mPa s)	Conductivity (mS cm^{-1})	Initial discharge capacity (mAh g^{-1})	Initial coulombic efficiency
[MEMBu$_3$P$^+$][TFSA$^-$]	86	1.4 ± 0.2	3450	86%
[PP13$^+$][TFSA$^-$]	117 [21]	1.7 ± 0.2	1900	85%
1 M LiClO$_4$/PC	2.5 [22]	4.9 ± 0.2	3390	78%
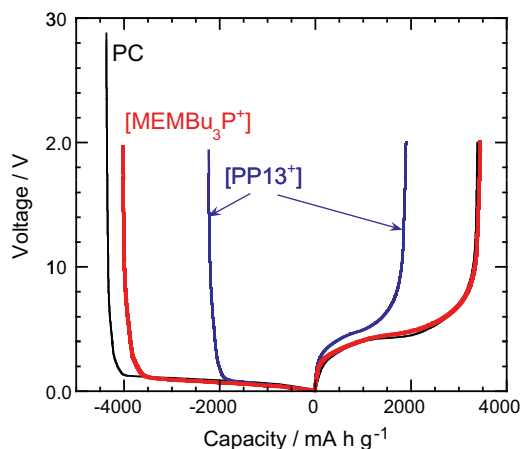
Fig. 2. Charge–discharge curves of Si GD-film electrodes at the first cycle in ionic liquids with cations of (a) [MEMBu$_3$P$^+$] and (b) [PP13$^+$], and in commercial organic solvent of (c) PC.

The electrode in PC solvent exhibited the coulombic efficiency of 78% at the first cycle. For the reason of the irreversible capacity in PC, it needs further consideration. There is one possibility that the irreversible capacity arose from a reductive decomposition of PC (C$_4$H$_6$O$_3$) forming lithium carbonate and propylene gas as following equation [23]:

$$C_4H_6O_3 + 4Li^+ + 4e^- \rightarrow 2Li_2CO_3 + C_3H_6 \qquad (1)$$
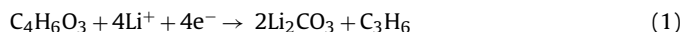
The reductive decomposition reaction takes place at the potential of approximately 0.7 V vs. Li/Li$^+$. However, no potential shoulder was observed at around 0.7 V in the charge curve. This result indicates that the reductive decomposition does not occur in the electrolyte using PC. We should note that higher coulombic efficiencies of 86% and 85% were achieved in the cases of the ionic liquids with [MEMBu$_3$P$^+$] and [PP13$^+$] as described in Table 1. The electrode reactions of the alloying/dealloying can proceed more efficiently in the ionic liquids. These results clearly reveal that the novel ionic liquid of [MEMBu$_3$P$^+$][TFSA$^-$] acts as a promising solvent for Si anode in Li-ion battery, like the commercial ionic liquid of [PP13$^+$][TFSA$^-$] [16].

Fig. 3 compares Nyquist plots (Z' vs. Z'') where Z' and Z'' refer to the real and imaginary parts of the cell impedance, which was obtained by the electrochemical impedance measurements for the Si thick-film electrodes at the charged state in the frequency range of 20 kHz to 10 mHz. The insets show enlarged views at higher frequency sides. In the electrolyte using PC, the Nyquist plots contain a small flattened semicircle in high frequency region and a large semicircle followed by a slope of Warburg impedance in low frequency region as shown in Fig. 3(a). The small flattened semicircle corresponds to an impedance of Li ion migration in an organic film layer on the electrode. Thus, the small semicircle implies the formation of the organic film layer in PC. In contrast, no small semicircle was detected in the ionic liquids as shown in the insets of Fig. 3(b) and (c). As suggested in the consideration with these high coulombic efficiencies, the ionic liquids are expected to promote more efficiently electrochemical reduction/oxidation of Li ions without the formation of the organic film layer. The diameter of the larger semicircle indicates a faradaic charge-transfer resistance R_{ct} based on the electrochemical reduction/oxidation of Li ions on the electrode surface. The R_{ct} of 190 Ω in the presence of [PP13$^+$] is approximately one-and-a-half times as high as that of about 120 Ω in cases of PC and [MEMBu$_3$P$^+$]. It is suggested that the smaller initial discharge capacity of 1900 mAh g^{-1} is caused by a suppression of the charge-transfer in the ionic liquid with [PP13$^+$] in comparison with other electrolytes.

At a higher current density, charge–discharge tests were performed as an additional experiment. In case of [PP13$^+$] cation, the initial discharge capacity was slightly reduced from 1900 to 1620 mAh g^{-1} with increasing the current density from 0.1 C to 0.25 C. The good rate performance is possibly attributed to an excellent stability of [PP13$^+$] cation against a reductive decomposition. On the other hand, in the ionic liquid using [MEMBu$_3$P$^+$] cation, we observed a drastic decay of the initial capacity from 3450 to 640 mAh g^{-1} with increasing the C rate. In both cases, smaller initial capacities were obtained at higher current densities. This result indicates that the charge-transfer resistance affects the discharge capacity.

Fig. 4 represents a dependence of the discharge capacity on the cycle number for the Si electrodes in the ionic liquids with [MEMBu$_3$P$^+$] and [PP13$^+$] cations. For comparison, the discharge capacity of the electrode in PC is also plotted in this figure. The
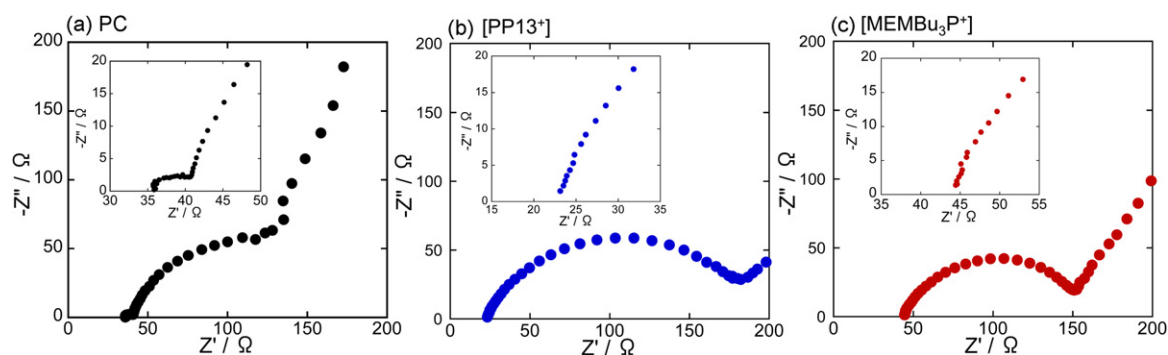
Fig. 3. Nyquist plots of Si GD-film electrodes in (a) PC and ionic liquids with cations of (b) [PP13$^+$] and (c) [MEMBu$_3$P$^+$] in charge charged state at 0.005 V vs. Li/Li$^+$ at the first cycle. The insets show enlarged views at higher frequency sides.
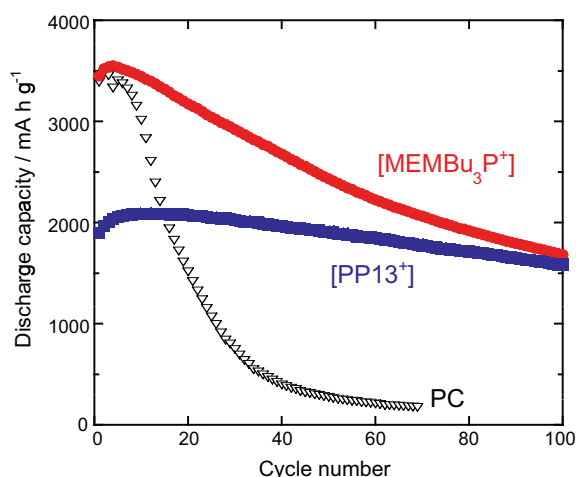
Fig. 4. Dependence of discharge capacity on cycle number for Si GD-film electrodes in ionic liquids with cations of (a) [MEMBu$_3$P$^+$] and (b) [PP13$^+$], and in commercial organic solvent of (c) PC.

discharge capacity in PC drastically dropped down with increasing the cycle number, and reached 200 mAh g^{-1} at 60th cycle. The significant capacity decay is attributed to a collapse and an electrical isolation of Si induced by its significant volumetric change. On the other hand, in each case of the ionic liquids using [MEMBu$_3$P$^+$] and [PP13$^+$], the capacity over 1500 mAh g^{-1} was maintained throughout 100 cycles. In particular, the ionic liquid with [PP13$^+$] exhibited a high capacity retention of 84% at the 100th cycle though its first discharge capacity of 1900 mAh g^{-1} is not so large. From these results, we can see that two kinds of the ionic liquids used in this study have a notable function as electrolytes to alleviate effectively the collapse and electrical isolation.

Fig. 5 displays SEM images of the Si electrodes as prepared and after charge–discharge cycling in PC and the ionic liquid with [MEMBu$_3$P$^+$]. The electrode before the cycling shows a smooth surface of the thick film (Fig. 5(a)). After the cycling in PC, a pulverized surface and large particles with a size over 10 μm were observed on the electrode (Fig. 5(b)). We can easily deduce the collapse and the electrical isolation in PC from the image. On the contrary, the surface was relatively smooth after cycling in the ionic liquid with [MEMBu$_3$P$^+$] though smaller particles were formed by the volumetric changes as shown in Fig. 5(c). These results have clearly demonstrated that the Si electrode in the ionic liquid with [MEMBu$_3$P$^+$] exhibits not only the large initial discharge capacity

but also the excellent cycling performance because the ionic liquid can effectively suppress the collapse and the electrical isolation during the cycling.

4. Discussion

The lower initial coulombic efficiency in case of PC can be explained in relation to a degree of a desolvation in the electrolyte. A solvation of Li ions by polar molecules is more easily performed in a solvent with increasing the dielectric constant of the solvent because the solvation is caused by a coulombic interaction between Li ions and polar molecules. It has been reported that the dielectric constant of PC is 64 at room temperature, and that Li ions are surrounded by PC molecules with the solvation number of 2.2 to form a shell-like solvation configuration which is very stable [24]. On the other hand, values of the dielectric constant have not accurately measured for the two kinds of the ionic liquids used in this study. Grätzel et al. have measured the dielectric constants for various ionic liquids such as 1-ethyl-2,3-dimethylimidazolium bis((trifluoromethyl)sulfonyl)amide, and reported that the dielectric constants of ionic liquids containing [TFSA$^-$] anion exhibited are lower than 10 [25]. In general, ionic liquids have much smaller dielectric constants in comparison with polar organic solvents in spite of molecules of the ionic liquids are positively or negatively charged [25], which is one of the most unique properties of ionic liquids. We can suggest that the ionic liquids used in this study have much smaller dielectric constants. Although Li ions are solvated by two [TFSA$^-$] anions by the coulombic interaction [26], it is considered that suggest the solvation can easily dissociate owing to their smaller dielectric constants. Therefore, the high coulombic efficiencies were achieved in the ionic liquid. On the other hand, the stably solvated Li ions, which cannot contribute to the electrode reactions, are accumulated on the electrode in PC with much higher dielectric constant.

The initial discharge capacity in the case of [MEMBu$_3$P$^+$] cation was much larger than that in the case of [PP13$^+$] cation even though these ionic liquids consist of the same anion of [TFSA$^-$]. The larger discharge capacity is presumably due to a smooth charge transfer of Li$^+$ ions at interface between the electrode surface and the electrolyte, rather than its slightly lower viscosity. The cations of [MEMBu$_3$P$^+$] and [PP13$^+$] accumulate on the surface of Si anode to compensate the charge, and form Helmholtz layer. The Li$^+$ ions are solvated by two [TFSA$^-$] anions in the electrolyte by the coulombic interaction, which forms a layer of negatively charged clusters [Li(TFSA)$_2$]$^-$ [26] on surface of Helmholtz layer. In the electrode reactions of Li$^+$ ions on the Si anode, an activation energy of des-
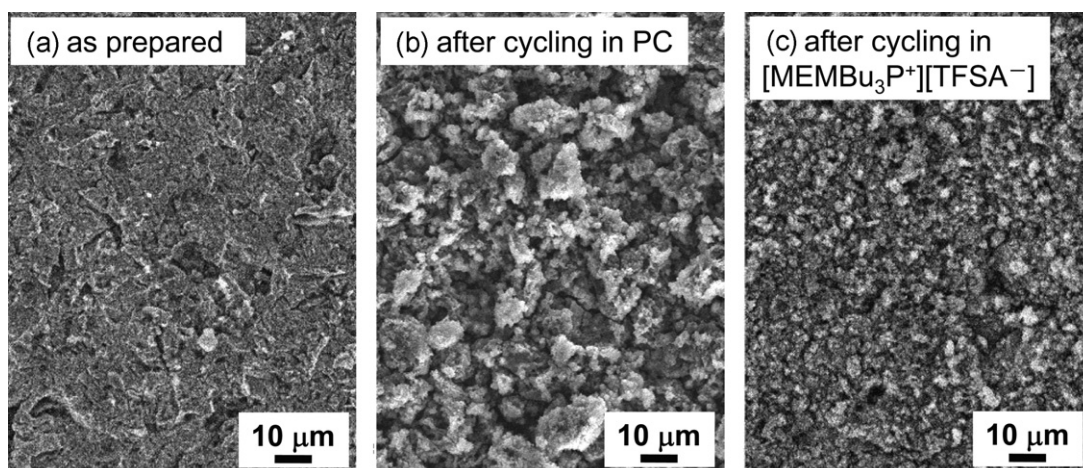
Fig. 5. SEM images of Si GD-film electrodes (a) as prepared and after charge–discharge cycling in (b) PC and (c) ionic liquid with [MEMBu$_3$P$^+$].

olvation is required to dissociate the $[Li(TFSA)_2]^-$. We speculate that an easier desolvation allows the electrode reaction to proceed efficiently because the activation energy can be reduced due to its local negative charge of ether groups by a polar covalent bond in $[MEMBu_3P^+]$ cations. In contrast, the desolvation of $[Li(TFSA)_2]^-$ is more difficult in the ionic liquid of $[PP13^+]$ which does not contain locally negative charge in the cation. An insufficient supplement of Li ions for the electrode reaction is supported by the higher charge-transfer resistance in the EIS measurements. Thus, the initial discharge capacity is suggested to be suppressed in the ionic liquid of $[PP13^+]$.

The origin of difference in the cycling performance is an electrical contact between the electrode and the electrolyte. An active material of Si cannot intrinsically avoid to be pulverized in any electrolytes owing to its volumetric change during alloying/dealloying reactions of Li–Si. The phenomenon leads to the electrode collapse and the electrical isolation between the active material and the substrate, which significantly reduces a proportion of Si contributing the alloying reaction to the total amount of Si active material. For this reason, the discharge capacity of Si anodes fades away by repeating the alloying/dealloying reactions. In PC solvent, Li ions solvated by PC molecules are not completely desolvated and accumulate to form the organic film layer on the electrode, which partially disturbs the electrode reaction. As a result, the alloying/dealloying reactions occur in the limited area on the Si electrode. Therefore, the collapse and the electrical isolation are enhanced, resulting in the capacity decay being accelerated. By contrast, we consider that the excellent cycling performance was exhibited in the ionic liquids used in this study because these electrolytes are resistant to form the organic film layer and can keep the electrical contact good. These considerations are based on the results of EIS (Fig. 3) and SEM (Fig. 5). The $[MEMBu_3P^+]$ cation has two ether groups with local negative charge by a polar covalent bond. We consider that the local negative charges enable efficient electrode reaction, resulting in the very large initial capacity. However, we should note that the very large capacity indicates a drastic volume change during charge–discharge reactions. Thus, it is suggested that the discharge capacity and the capacity retention rapidly faded away in case of $[MEMBu_3P^+]$ cation.

5. Conclusion

The thick film electrodes of Si were prepared by the gas-deposition method as the anode, and, the applicability of the novel ionic liquid consisting of 1-methoxyethoxymethyl(tri-*n*-butyl)phosphonium $[MEMBu_3P^+]$ cation and bis(trifluoro-methanesulfonyl)amide $[TFSA^-]$ anion was investigated as the electrolyte of Li-ion battery using the Si thick-film electrode. For comparison, we also used the commercial ionic liquid consisting of 1-methyl-1-propylpiperidinium $[PP13^+]$ cation and the anion, and the typical organic solvent of PC. The electrochemical properties and electrode performance in the solvents were studied by the constant current charge–discharge test, the EIS measurements, and the SEM observations. These ionic liquids containing $[MEMBu_3P^+]$ and $[PP13^+]$ cations exhibited notable coulombic efficiencies of 86%

and 85% at the first charge–discharge cycle. The initial discharge capacity of 3450 mAh g^{-1} and excellent cycling performance were achieved in the ionic liquid with $[MEMBu_3P^+]$. On the other hand, the commercial ionic liquid with $[PP13^+]$ showed very high capacity retention of 84% at the 100th cycle though the initial discharge capacity of 1900 mAh g^{-1} is not so large. The novel ionic liquid was confirmed to effectively suppress the collapse and the electrical isolation induced by the pulverization during the charge–discharge cycling. The excellent performance is possibly attributed to more effective desolvation of Li ions from the anions due to its lower dielectric constant compared with the propylene carbonate solvent.

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