Lithium-ion batteries are the most attractive power sources in terms of high voltage and energy density, and they are now widely employed not only as small sized batteries for mobile electronics but also as large-scale batteries for smart grids and commercially produced electric vehicles. In particular, the application to vehicles has resulted in an innovation of driving force of the vehicles. However, lithium-ion batteries cannot yet compete with gasoline as regards mileage because of their limited energy density. Therefore, there have been intensive efforts to develop new cathode active materials for lithium-ion batteries and new rechargeable batteries with a far higher energy density than the present lithium-ion batteries. One effective approach is to find a new type of battery system with a high energy density that is realized by charging and discharging accompanied by multiple ion transportation.

Batteries containing an Al anode and molten salt have been studied as one attractive option. Some battery systems have been expected that can operate via a reaction that involves the transfer of multiple chlorine ions. Knutz et al. have investigated the electrochemical properties of a battery with a nickel cathode, Al anode, and inorganic molten salts consisting of AlCl3 and NaCl at 175°C. Gilbert and Osteryoung have investigated the electrochemical properties of nickel in inorganic molten salts consisting of AlCl3 and KCl at 175–210°C. On the other hand, the electrochemical properties of molten salts consisting of AlCl3 and organic salts have also been widely studied. The melting points of such chloroaluminate salts change when the ratio of AlCl3 and organic salts is changed, and they decrease to around room temperature, although their ion conductivity is reported to be well maintained. Accordingly, there have been many studies of the electrochemical properties of chloroaluminate salts with organic salts at around 100°C or ambient temperature in relation to battery applications and the electro deposition of metals and sensors. Koura et al. have studied the electrochemical properties of Al/FeS2 and Al/polyaniline batteries containing AlCl3-1-butylpyridinium chloride or AlCl3-1-ethyl-3-methylimidazolium chloride (EMIC) at ambient temperature or 100°C. They tried to improve the cell performance by adopting an alloy anode, and by introducing additives to molten salts.

Batteries have been reported that consist of AlCl3-EMIC electrolyte and cathode active materials Li+ ion intercalated against Al anode have been reported. Jayaprakash et al. have investigated the charge/discharge performance of a battery with a V9O35 nano-wire cathode, and it delivered 305 mAh g⁻¹ at the first discharge and 273 mAh g⁻¹ at the 100th discharge. Lin et al. introduced an Al/graphite battery containing AlCl3-EMIC electrolyte. The battery produced only 70 mAh g⁻¹ but it afforded one-minute charging at a very high rate of 4 A g⁻¹ and withstood over 7500 cycles. In addition, batteries with metal chloride cathodes have been investigated.

With such electrolytes containing AlCl3 and organic salts, the composition and concentration of ions related to aluminum vary greatly depending on the AlCl3/organic salt ratio, and this affects the reversibility of the dissolution and deposition of cathode active materials. We therefore selected vanadium chloride as the cathode active material and investigated its oxidation and reduction in AlCl3 and EMIC. The theoretical energy density of Al/VCl3 based on trivalent redox reaction of Al + VCl3 ⇌ AlCl3 + V is not large, 177.1 Wh kg⁻¹ and 523.1 Wh L⁻¹. However, VCl3 and V are insoluble into the AlCl3/EMIC molten salt, which means that VCl3 and V are optimum to estimate oxidation and reduction as cathode active materials for aluminum batteries containing AlCl3 and organic molten salt. Vanadium chloride has been investigated as an active material for all-vanadium redox flow batteries. However, the electrochemical properties of the material have not been investigated in detail for application to cathodes for batteries containing an Al anode and an AlCl3 organic salt electrolyte. Hanz et al. have investigated complexes of VCl3 and VCl4 in AlCl3-1-ethyl-3-methylimidazolium chloride ratio where NiCl2 was deposited on the electrode after Ni oxidation. They indicated the possibility of realizing a rechargeable battery with an Al anode, a NiCl2 cathode, and AlCl3 combined with an organic molten salt.

This paper describes the change in the electrochemical properties of vanadium chloride in molten salt containing AlCl3 and 1-ethyl-3-methylimidazolium chloride (EMIC) with a molar ratio of 1.5/1.0 at an ambient temperature using cyclic voltammetry and the X-ray absorption near-edge structure (XANES). Cyclic voltammograms (CVs) of VCl3 contain a pair of oxidation peak at about 1.5 V vs. Al/Al³⁺ and reduction peak at about 0.9 V vs. Al/Al³⁺ assigned to the V(3) ⇌ V(2) reaction and a pair of oxidation peak at about 0.9 V vs. Al/Al³⁺ and reduction peak at about 0.4 V vs. Al/Al³⁺ assigned to the V(2) ⇌ V(0) reaction. The former remains in the CV after reduction and oxidation cycling. On the other hand, the latter disappears from the CV after a couple of cycles. We also investigated the effect of adding fluorobenzene (FB) to the AlCl3-EMIC salts on the solubility and electrochemical properties of VCl3. FB greatly reduces the VCl3 dissolution in the salts and improves capacity retention with reduction and oxidation cycling without change in the reaction process.

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Received January 18, 2016; Published February 10, 2016.

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discharging as a secondary battery. Additionally, we studied a way of improving the discharge capacity during charge/discharge cycles by controlling the solubility of vanadium chloride using fluorobenzene as an electrolyte additive.

Experimental

All the electrolytes and electrodes were prepared under inert gas and dry conditions. O₂ content less than 1 ppm and dew point less than −85 °C inside a 5N Ar-filled glove box.

Electrolytes.—Before preparing the electrolytes and electrodes, we thoroughly dried 1-ethyl-3-methylimidazolium chloride (EMIC, Kanto Chemical or Toyo Gosei) in a vacuum at 100 °C for at least three days. Then electrolytes containing AlCl₃ (99.999% anhydrous, Aldrich) and EMIC were prepared by adding AlCl₃ in small doses to EMIC, which was being stirred in a Duran glass vial to avoid heat generation. We then dehydrated the electrolytes by immersing a polished Al wire (99.999% and 1.0 mm diameter, Nilaco) in them for two weeks or longer, and additionally by immersing Pt wires to apply a voltage of 1.0 V. We checked the color of the electrolytes prepared with the procedures described above, and used only those that were colorless or very pale yellow since we considered them to be sufficiently pure. In addition, we checked the dehydration of the electrolytes by cyclic voltammetry to confirm that there were no current peaks in the 0–1.9 V range vs. Al/Al³⁺ and no incline in the baselines of the cyclic voltammograms.

Electrodes.—We used metal wire or plate electrodes, or prepared compound mixture electrodes.

Metal electrodes.—We cut a vanadium plate (99.7% and 0.8 mm thick, Nilaco) into a square with 5 mm sides and welded it to Pt wire (99.98% and 1.0 mm diameter, Nilaco) for use as a working electrode (or positive electrode). An aluminum plate (99.999% and 0.1 mm thick, Nilaco) and wire (99.999% and 1.0 mm diameter, Nilaco) were used as negative electrodes and references, respectively. Before being used, the surfaces of the vanadium and aluminum plates were polished with #600-1000 emery paper and the surface of the aluminum wire was washed and shaved with the edge of a ceramic brick before the measurements. Additionally, a composite electrode of vanadium flake was prepared with a P-6 ball mill (Fritsch) operating at 600 rpm for over 10 hours and mixed with acetylene black and PTFE powder, which is the same method as that used for the compound mixture electrode described below.

Compound mixture electrodes.—We mixed vanadium (II) chloride (85%, Aldrich) or vanadium (III) chloride (99%, Merck), acetylene black (HS-100, Denki Kagaku Kogyo), and PTFE powder (DuPont-Mitsui Fluorochemicals) with a 6:3:1 weight ratio for over 10 hours and mixed with acetylene black and PTFE powder, which is the same method as that used for the compound mixture electrode described below.

Electrochemical measurements.—We set working, counter, and reference electrodes and poured the electrolyte into an inverted conical glass vessel and sealed it to form a test cell. Test cells were placed in an argon-filled glove box for cyclic voltammetry, electrochemical impedance measurements, and chronopotentiometry. An electrochemical measuring system 1255WB (Solartron), and potenti/galvanostats SP-200 and SP-300 (Bio-Logic) were used for the measurements.

Analysis of electrodes and electrolytes.—The test electrodes were washed twice with acetonitrile dehydrated below 10 ppm (Kishida Chemical) and dried. The samples were analyzed without exposing them to air. The solubility and change in composition of the electrolytes after charge/discharge cycling were measured with inducively coupled plasma mass spectroscopy (ICP-MS) (Agilent 7500cx). The sample for the solubility test was prepared as follows. An AlCl₃-EMIC molten salt with a molar ratio of 1.5/1.0 and fluorobenzene (99.5% and moisture of 30 ppm or less, Kishida Chemical) added AlCl₃-EMIC salt were saturated with vanadium chloride. The solution was centrifuged at 6000 rpm for 5 min, and then passed through a syringe filter with 200 μm pores, and diluted 10,000 or 100,000 times with 0.1 mole L⁻¹ nitric acid, for use in ICP-MS measurements. V K-edge X-ray absorption fine structure (XAFS) measurements were performed at the BL14B2 beamline of SPring-8, Hyogo Pref., Japan. The X-ray absorption spectra at the V K-edges of the electrodes after electrochemical measurements as well as VCl₂ (85%, Aldrich) and VCl₃ (99%, Merck) as the references were measured.

Results and Discussion

The electrochemical properties of vanadium complexes in EMIC rich (basic) AlCl₃-EMIC salts have been investigated in detail by Hanz and Riechel. Vanadium chlorides have to be dissolved in the salts and deposited on the electrode through discharging and charging if they are to function as cathode active materials for secondary batteries. However, Nakaya et al. have reported that active metal chloride materials are difficult to deposit via oxidation in basic molten salt. We then investigated the electrochemical properties of vanadium chloride in AlCl₃ rich (acidic) AlCl₃-EMIC salt.

Figure 1 shows cyclic voltammograms (CVs) of vanadium plate and composite electrodes in AlCl₃-EMIC at 0.5 mV s⁻¹. The electrodes both had CVs with the main current peaks at nearly the same potential, oxidation peaks at about 1.2 V vs. Al/Al⁺ and 1.45–1.5 V vs. Al/Al⁺, and a reduction peak at 0.95–1.05 V vs. Al/Al⁺. The oxidation peak at about 1.2 V vs. Al/Al⁺ initially increased and then diminished for the V plate. The corresponding peak for the composite electrode almost disappeared after the 2nd cycle. The oxidation peak at 1.45–1.5 V vs. Al/Al⁺ is sharp and strong for the composite and weak and broad for the plate, and it increased in size with cycling. The reduction peak at 0.95–1.05 V vs. Al/Al⁺ also increased through cycling for both electrodes, which suggests that it forms a pair with the oxidation peak at 0.95–1.05 V vs. Al/Al⁺. Moreover, a purple solid was precipitated at the bottom of the cell during the potential cycle, indicating that vanadium chloride is formed by the electrochemical oxidation of vanadium metal. Tsuda et al. reported the electrochemical reaction of solvated VCl₂ in AlCl₃-EMIC with a molar ratio of 1.5/1.0, where they found similar precipitates which formed by irreversible oxidation to VCl₃ due to its low solubility.

![Figure 1. Cyclic voltammograms of vanadium plate (black) and composite (red) electrodes with Al counter and reference electrodes in an AlCl₃-EMIC molten salt with a 1.5/1.0 molar ratio at a sweep rate of 0.5 mV s⁻¹ and at room temperature.](image-url)
The matching suggests that VCl₃ is produced by the redox cycling of vanadium metal within the measured potential window.

We also prepared composite electrodes containing solid VCl₃, acetylene black (AB), and PTFE powder and used them for cyclic voltammetry and charge/discharge tests. Cyclic voltammograms of a VCl₃ composite electrode in AlCl₃-EMIC salt are shown in Fig. 2. The CVs for the 1st to 4th sweeps contain a large oxidation peak at about 0.9 V vs. Al/Al³⁺ and a large reduction peak at 0.4 V vs. Al/Al³⁺. There is also a more negative potential as well as oxidation peaks at about 1.2 V vs. Al/Al³⁺ and at 1.45–1.55 V vs. Al/Al³⁺ and a reduction peak at about 0.9 V vs. Al/Al³⁺, which can be seen in the CVs of vanadium electrodes in Fig. 1. However, the additional peaks disappear only and the oxidation and reduction peaks at 1.45–1.55 V vs. Al/Al³⁺ and at about 0.9 V vs. Al/Al³⁺ in the CVs of the VCl₃ composite electrode remain after the charge/discharge tests. As for the oxidation peak at about 1.2 V vs. Al/Al³⁺, Hanz et al. have attributed the peak at 1.23 V vs. Al/Al³⁺ in EMIC rich (basic) AlCl₃-EMIC salt to the following reaction:²⁹

\[
\text{VCl}_5^{-} \rightleftharpoons \text{VCl}_3^{2-} + \text{e}^{-} \quad [1]
\]

There is no guarantee that the same reaction also proceeds at about 1.2 V vs. Al/Al³⁺ in our acidic salts, but their speculation suggests that the oxidation peak relates to complex ions containing vanadium.

Figure 3 shows potential profiles against the specific capacity of the VCl₃ composite electrode obtained by cyclic chronopotentiometry at a reduction and oxidation current of 3.33 mA g⁻¹ in a 0.1–1.75 V potential range vs. Al/Al³⁺. In Fig. 3, the initial capacity was 76 mAh g⁻¹, which was smaller than the theoretical value of 170 mAh g⁻¹. We supposed that the smaller value was due to the primitive VCl₃ electrode and/or unoptimized cell. However, we decided to use the cathodes and/or unoptimized cell. However, we decided to use the cathodes and reference electrodes in AlCl₃-EMIC molten salt with a 1.5/1.0 molar ratio at room temperature.

To confirm the electrochemical reaction concerning V(2), we prepared VCl₂ composite electrodes and measured the cyclic voltammetry. Figure 4 shows the results. In the measurements, we set the potential range so that it was more negative than 1.4 V vs. Al/Al³⁺ to avoid the formation of V(3) or compounds with a higher vanadium valence. The reduction current increased at a potential more negative than 0.6 V vs. Al/Al³⁺, and a small oxidation peak at around 0.7 V vs. Al/Al³⁺ was observed only in the first sweep. No reduction peak was observed at about 0.9 V vs. Al/Al³⁺. The reduction current at a potential more negative than 0.6 V vs. Al/Al³⁺ suggests the reduction of V(2) → V(0). The fact that there were no reduction peaks at around 0.9 V vs. Al/Al³⁺ indicates that no VCl₃ formed in our measurement system, which confirms that the reduction peak at about 0.9 V vs. Al/Al³⁺ in Fig. 2 corresponds to the reduction of V(3) → V(2).

We confirmed the products that remained on the electrodes after the reaction by using V K-edge XAFS measurements. The VCl₃ and VCl₃ composite electrodes were reduced in AlCl₃-EMIC salt with a molar ratio of 1.5/1.0 by performing a linear sweep at 0.5 mV s⁻¹ from 0.9 V vs. Al/Al³⁺ and at 0.4 V vs. Al/Al³⁺ corresponds to V(2) ⇔ V(0), based on the potential at onset in the CVs in Figs. 1 and 2 and the ocp of VCl₃ (about 1.43 V vs. Al/Al³⁺) and VCl₂ (about 1.2 V vs. Al/Al³⁺). From the chronoaomperometric features, the reaction of V(2) ⇔ V(0) at a lower voltage in the first cycle was superseded by the higher voltage reaction, V(3) ⇔ V(2), after the second cycle, and this is consistent with the CVs in Fig. 2.

The pair of oxidation and reduction peaks at 1.45–1.55 V vs. Al/Al³⁺ and at about 0.9 V vs. Al/Al³⁺ corresponds to the reaction of V(3) ⇔ V(2), and the pair of oxidation and reduction peaks at about 0.9 V vs. Al/Al³⁺ and at 0.4 V vs. Al/Al³⁺ corresponds to V(2) ⇔ V(0), based on the potential at onset in the CVs in Figs. 1 and 2 and the ocp of VCl₃ (about 1.43 V vs. Al/Al³⁺) and VCl₂ (about 1.2 V vs. Al/Al³⁺). From the chronoaomperometric features, the reaction of V(2) ⇔ V(0) at a lower voltage in the first cycle was superseded by the higher voltage reaction, V(3) ⇔ V(2), after the second cycle, and this is consistent with the CVs in Fig. 2.

Figure 2. Cyclic voltammograms of VCl₃ composite electrode at the 1st and 2nd (black), the 3rd and 4th (red) sweeps and after oxidation and reduction cycling (blue) at a sweep rate of 0.5 mV s⁻¹ and at room temperature for a system with Al as counter and reference electrodes in AlCl₃-EMIC molten salt with a 1.5/1.0 molar ratio.

Figure 3. Potential profiles of a VCl₃ composite electrode against specific capacity during cyclic chronopotentiometry at 3.33 mA g⁻¹ in a 0.1–1.75 V potential range vs. Al/Al³⁺ for 10 reduction and oxidation cycles for a system with Al as counter and reference electrodes in AlCl₃-EMIC molten salt with a 1.5/1.0 molar ratio at room temperature.

Figure 4. Cyclic voltammograms of a VCl₂ composite electrode at the 1st (black) and 2nd (red) sweeps at a sweep rate of 0.5 mV s⁻¹ and at room temperature for a system with Al as counter and reference electrodes in AlCl₃-EMIC molten salt with a 1.5/1.0 molar ratio.
Potential / V vs. Al/Al\textsuperscript{3+} 
Current density / mA cm\textsuperscript{-1} 

$\text{VCl}_3$  
$\text{VCl}_2$

Figure 5. Linear sweep voltammograms for $\text{VCl}_3$ (black) and $\text{VCl}_2$ (red) composite electrodes against Al electrodes as a counter and reference in AlCl\textsubscript{3}-EMIC with a molar ratio of 1.5/1.0 reduced to 0.3 V vs. Al/Al\textsuperscript{3+} at 0.5 mA s\textsuperscript{-1}.

ocp to 0.3 V vs. Al/Al\textsuperscript{3+}, followed by reduction at a constant potential of 0.3 V vs. Al/Al\textsuperscript{3+} for 72 h. Then the electrodes were washed twice with 1, 2-dichloromethane and dried at room temperature in a vacuum overnight or longer, and then used as the samples for the XAFS measurements. The linear sweep voltammograms (LSVs) of $\text{VCl}_2$ and $\text{VCl}_3$ composite electrodes are shown in Fig. 5. We observed two main steps in the reduction current increase in both LSVs; the first step consisted of a gradual increment around 1.1–0.8 V Al/Al\textsuperscript{3+} and the second step was a sudden increment at 0.55 V vs. Al/Al\textsuperscript{3+}, corresponding to the onset potentials of the reduction current peaks of the CVs in Figs. 2 and 4.

Figure 6 shows V K-edge XANES spectra for the $\text{VCl}_3$ composite electrodes before and after a 0.3 V reduction, along with the references. Before reduction, the spectra overlapped that for the $\text{VCl}_3$ reference. On the other hand, the edge energy for the electrode after a 0.3 V reduction shifted about 1 eV lower, and the edge shape resembled that for the $\text{VCl}_2$ reference in the 5469–5472 eV range, which suggests that after a 0.3 V reduction the electrode contained $\text{VCl}_2$ as the reaction product.

Figure 7 shows V K-edge XANES spectra for $\text{VCl}_2$ composite electrodes before and after a 0.3 V reduction with $\text{VCl}_2$ as a reference. The spectra for the electrode before reduction well overlaps that for the $\text{VCl}_2$ reference. After a 0.3 V reduction, the edge shifts 1 eV in energy in the range above 5470 eV. This shift suggests that the $\text{VCl}_2$ in the electrode is partly reduced to vanadium metal although we did not obtain the vanadium metal spectrum because the vanadium foil was too thick for X-ray transmission. Our XAFS results for the $\text{VCl}_2$ composite electrode indicate that vanadium metal produces 0.3 V vs. Al/Al\textsuperscript{3+} after reduction. Therefore, the reduction to 0.3 V vs. Al/Al\textsuperscript{3+} for the $\text{VCl}_3$ electrode may also produce vanadium metal.

In general, when metal chlorides are applied to batteries as cathode active materials, their high solubility in the electrolyte often suppresses battery performance. We therefore investigated fluorobenzene (FB) as a poor solvent against vanadium chloride and the effect of its addition to the molten salt on the electrochemical properties. Figure 8 shows the $\text{VCl}_3$ solubility dependence measured by ICP-MS for the FB content of FB added AlCl\textsubscript{3}-EMIC (molar ratio of 1.5/1.0) salts. $\text{VCl}_3$ dissolves completely at $1980 \mu$ mole L\textsuperscript{-1} in AlCl\textsubscript{3}-EMIC and at around 50 $\mu$ mole L\textsuperscript{-1} in FB. Once FB was added to AlCl\textsubscript{3}-EMIC salts, the solubility greatly decreased to the 4–15 $\mu$ mole L\textsuperscript{-1} range against FB/(FB + AlCl\textsubscript{3}-EMIC) with a molar ratio of 0.01/1.0-0.8/1.0. Furthermore, the dependence is unusual; the addition of FB in a minuscule amount suddenly reduced the $\text{VCl}_3$ solubility in the salt, and the solubility remained low for an FB content ratio of 0.8/1.0, and could be less depending on the FB content. The above suggests that FB does not change the dissociation activity of $\text{VCl}_3$ in bulk of the
salts but only at the interface between the surface of the VCl₃ particles and the salts, and so further investigation is needed.

Figure 9 shows CVs of a Pt electrode in AlCl₃-EMIC electrolyte containing different FB ratios of FB/(FB+AlCl₃-EMIC) of 0.5/1.0, 0.91/1.0, and 0.99/1.0. A pair of redox peaks crossing at 0 V vs. Al/Al³⁺ and corresponding to the dissolution and deposition of Al on the Pt electrode, does not change its potential, but the peak currents differ. The result reveals that the addition of FB to the electrolyte seems to affect the activity of the redox species for Al, but does not change the reaction process.

Figure 10 shows CVs of V plate against Al as a reference and counter electrodes in AlCl₃-EMIC (1.5/1.0) salt containing FB with a molar ratio of FB/(FB+AlCl₃-EMIC) = 0.8/1.0, after certain activation of the V surface electrochemically. The two oxidation peaks at 1.3 and 1.6 V vs. Al/Al³⁺, and the small reduction peak at 1.0 V vs. Al/Al³⁺ correspond to the three peaks in the CV for V plate in the electrolyte without FB, shown in Fig. 1. However, two oxidation peaks corresponding to those at 1.2 V and 1.45–1.5 V vs. Al/Al³⁺ in Fig. 1, shifted slightly in the positive direction. This shift implies that FB addition prevented vanadium dissolution, and resulted in a delay in the oxidation reaction, whereas the basic electrochemical reaction process from V metal to V(2) and V(3) was preserved.

Figure 11 shows CVs of VCl₃ composite electrodes in FB added AlCl₃-EMIC (1.5/1.0) with a molar ratio of FB/(FB+AlCl₃-EMIC) = 0.8/1.0 at the first sweep and after reduction and oxidation cycling. The CV at the 1st sweep contains a large oxidation peak at about 0.9 V vs. Al/Al³⁺ and a large reduction peak at 0.4 V vs. Al/Al³⁺ as well as oxidation peak at about 1.5 V vs. Al/Al³⁺ and a reduction peak at 0.8–0.9 V vs. Al/Al³⁺, which are also observed in FB free salt, as shown in Fig. 2. This again suggests that FB does not change the reaction process. However, as shown in Fig. 11, the addition of FB caused the oxidation peak at around 1.25 V vs. Al/Al³⁺ to disappear and only a small shoulder is observed at about 1.15 vs. Al/Al³⁺ in the first CV. If the peak indicates a reaction related to complex ions containing vanadium such as Reaction 1 described above, FB suppressed VCl₃ solubility and the formation of vanadium complex ions, which resulted in a decrease in peak current. In fact, many FB and transition metal complexes including vanadium ion have been reported. FB may interact with VCl₃ on the surface of the cathode to hinder its dissolution into the salt.

Reduction and oxidation potential profiles obtained by the cyclic chronopotentiometry of a VCl₃ composite electrode in FB added AlCl₃-EMIC salt are shown in Fig. 12. The profiles in Fig. 12 are basically the same as those obtained in FB free salt shown in Fig. 3. The change in capacity with cycle number is shown in Fig. 13 for the AlCl₃-EMIC salt with and without FB. The addition of FB improved capacity retention. Although capacity fading remains, mainly due to the disappearance of V(2) as a result of the cyclic redox process, the increasing retention of capacity explains the effect of FB via stemming the dissolution of VCl₃ from the electrode.
investigation will elucidate the reason for the disappearance of the V(2) ↔ V(0) process, which is a key to improving the charge and discharge capacity of the Al-VCl3 system.

Conclusions

We studied the electrochemical properties of vanadium chloride in molten salt containing AlCl3 and 1-ethyl-3-methylimidazolium chloride (EMIC) with a molar ratio of 1.5/1.0 at ambient temperature. We also investigated the effect of the addition of fluorobenzene (FB) as a poor solvent to the AlCl3-EMIC salts on the solubility and electrochemical properties of vanadium chloride. Cyclic voltammetry revealed the reaction process and XANES spectra helped identify the reaction products. The results we obtained can be summarized as follows:

1. Cyclic voltammograms (CVs) of VCl3 in the 0.3–1.8 V potential range vs. Al/Al3+ contain two pairs of oxidation peaks at about 1.5 V vs. Al/Al3+ and a reduction peak at about 0.9 V vs. Al/Al3+. An oxidation peak at about 0.9 V vs. Al/Al3+ and a reduction peak at about 0.4 V vs. Al/Al3+. The former is assigned to the reaction of V(3) ↔ V(2) and can still be observed in the CV after 20 reduction and oxidation cycles. The latter is assigned to the reaction of V(2) ↔ V(0) and disappeared from the CV after a few cycles.

2. The corresponding reactions are also observed in the reduction and oxidation potential profiles of VCl3 at 3.33 mA g⁻¹ in the potential 0.1–1.75 V range vs. Al/Al3+. We observed a plateau at 1.1 V vs. Al/Al3+ in the reduction potential curves, which corresponds to the V(3) ↔ V(2) reaction, and is maintained in the reduction potential curve at the 10th cycle. We also observed a plateau at 0.6 V vs. Al/Al3+ in the first reduction potential curve, which is assigned to the V(2) ↔ V(0) reaction. However, it disappeared from the second reduction potential curve. VCl3 reversibly reduces to VCl2 while vanadium formed by the reduction of VCl3 hardly oxidizes to VCl3 in our AlCl3-EMIC molten salt. Thus, the monovalent reaction was found to take place after a few cycles in the Al/VCl3 cell, instead of multivalent reaction between V(3) ↔ V(0).

3. The dissolution of VCl3 in the AlCl3-EMIC salt was greatly reduced by the FB addition although the FB did not change the VCl3 reaction process. FB addition improved capacity retention with cycling.

Acknowledgments

This work was financially supported by the New Energy and Industrial Technology Development Organization (NEDO), Japan. The synchrotron radiation experiments were performed at the BL14B2 beamline of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2011A1800). We thank Professors Yoshiharu Uchimoto, and Hajime Arai, and Associate professor Masatsugu Oishi of Kyoto University for conducting the XANES measurements. We also thank Yoko Miyamoto for conducting the ICP-MS measurements, and Tooru Matsui of Panasonic Corp., Katsumori Nakaya, and Hiroshi Ogasa of Honda R&D Co. Ltd for advice and suggestions.

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Figure 13. Change in the specific capacity of a VCl3 composite electrode with cycle number at 3.33 mA g⁻¹ in a 0.1–1.75 V potential range vs. Al/Al3+ for 10 cycles against Al as reference and counter electrodes in AlCl3-EMIC molten salt with a 1.5/1.0 molar ratio containing fluorobenzene (FB) with FB/AlCl3-EMIC = 0.8/1.0, or without FB.