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<th>Oxidation of Nickel in AlCl3-1-Butylpyridinium Chloride at Ambient Temperature</th>
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Lithium-ion batteries are the most appealing power sources that operate at a higher voltage and achieve a higher energy density, compared with nickel metal-hydride batteries, and are now widely used in commercial hybrid electric vehicles. Lithium-ion batteries, however, are not competitive with gasoline engines to date because of their limited energy density. Therefore, intensive efforts have been done to develop new rechargeable batteries with far higher energy density than the present lithium-ion batteries. One effective approach to developing batteries with high energy density is to find a new type of cell systems that is charged and discharged accompanied by multiple-ions transport.

Nickel compounds have been expected to be one of the cathode active materials for high energy batteries. Nickel oxo-hydride, for example, has been used as a cathode active material for commercial nickel-cadmium and nickel-metal hydride batteries and also investigated as cathode active materials for other high energy batteries such as zinc-nickel batteries. Nickel compounds are also expected to be cathode active materials for high energy batteries having non-aqueous electrolytes. Lithium nickel oxides and their derivatives have also been expected to be cathode active materials for high energy density lithium-ion batteries.

Batteries having Al anode and molten salt have been studied as one appealing alternative. Some battery systems have been expected to operate by the reaction for plural chloride ion transfer. Knutz et al. operated a battery containing nickel cathode and inorganic molten salts consisting of AlCl3 and NaCl at 175 °C and studied its electrochemical properties. Gilbert et al. investigated the electrochemical properties of nickel in molten salts consisting of AlCl3 and KCl at 175–210 °C.

On the other hand, electrochemical properties for molten salts containing AlCl3 and organic salts have also been widely studied. Such chloroaluminate salts vary their melting points, decreasing to lower temperature as they approach, by changing the ratio of AlCl3 and organic salts. Few reports, however, have been reported in spite of several studies on reduction of NiCl2. Specifically, no reports relate any identified products deposited on the electrode by oxidizing Ni. The confirmation and identification of deposited products of nickel and nickel chloride after charging and discharging are very important to establish a practical Ni cathode for Al/Ni rechargeable cells.

It is also important to find an optimum Lewis acidity of AlCl3/organic salt to establish and repeat effective oxidation of nickel and reduction of nickel chloride because such reactions need supply and regeneration of chloride ions. We thus have studied oxidation of nickel to nickel chloride in detail in the molten salts consisting of AlCl3 and BPC in view of the influence of the properties of the molar ratio of the molten salts, especially in detailed acidic ones, to relate to the reversibility of the Ni electrode. We have made a significant point of confirming the product deposited on the electrode.
after oxidizing nickel and identifying the deposition as nickel chloride.

**Experimental**

Electrolytes and electrode solutions were prepared under inert gas and dry condition (O₂ content less than 3 ppm and dew point less than – 80 °C) inside an Ar-filled glove box.

**Electrolytes.—** Aluminum chloride (99.8%, Wako Pure Chemical Industries) and 1-butylpyridinium chloride (98%, Tokyo Chemical Industry) were dried under vacuum at 75 °C for 72 h. The electrolytes containing AlCl₃ and BPC with molar ratios of 0.8/1.0, 0.9/1.0, 1.0/1.0, 1.05/1.0, 1.1/1.0 and 1.5/1.0 were prepared by stirring in Teflon vessels to avoid generating heat. The electrolytes were dehydrated by immersion with polished Al wire (99.999% and 1.0 mm diameter, Nilaco) for two weeks or longer and we checked the purity of electrolytes by cyclic voltammetry using Pt electrode between 0.2 V and 1.8 V at a scan rate of 1.0 mVs⁻¹. No peaks of electrochemical reaction related to impurity were observed in the CV.

**Electrodes.—Nickel electrode A.—** 0.1 mm thick nickel plate (99%, Nilaco) was cut into pieces 5 mm wide and 10 mm long and welded to Ni wire (99.9% and 1.0 mm diameter, Nilaco) onto the plate to use as working electrodes. The surface of the electrodes was polished thoroughly before electrochemical measurements.

**Nickel electrode B.—** We used Ni powder (99.8%, Aldrich) and poly vinylidene fluoride (PVDF, HSV900, Arkema). Before use, Ni and PVDF powder was dried at 120 °C in a vacuum for 16 hours. We made PVDF 6 wt% solution with N-methyl-2-pyrrolidone dehydrated below 20 ppm (NMP, Kishida Chemical) previously and added Ni powder to the solution to be consistent with the weight ratio of Ni : PVDF = 9 : 1 and slurried. We coated this slurry onto Pt mesh (99.98%, 80mesh, Nilaco). The sheet was roll-pressed and cut after drying in a vacuum at 80 °C overnight. Then we welded 1.0 mm-diameter Ni wire to the cut Ni composite sheet to use as a positive electrode.

**Al electrode A.—** Counter and reference electrodes were prepared by polishing and coating Al wire (99.999% and 1.0 mm diameter, Nilaco) of 2 mm diameter and 10 mm long. **Al electrode B.—** As a negative electrode, 0.1 mm thick Al plate (99.999%, Nilaco) was cut into pieces 5 mm wide and 30 mm long. The surface of the electrodes was polished thoroughly before the experiment.

**Pt electrode.—** Pt wire (99.95% and 0.5 mm diameter, EC Frontier) was coiled in 2.5 mm diameter and 15 mm long and used as a working electrode for CVs to check existence of impurity in the molten salts, as described above.

**Solubility of NiCl₂ into AlCl₃/BPC electrolytes.—** We roughly estimated the NiCl₂ solubility into AlCl₃/BPC salts with AlCl₃/BPC molar ratios of 0.9/1.0, 1.0/1.0, and 1.5/1.0. We added 2.6 mg (0.001 mol l⁻¹) each of NiCl₂ powder into 20 ml of the electrolyte at 35 °C, followed by stirring for over 20 hours for the 1.0/1.0 and 1.5/1.0 ratio salts. For the 0.9/1.0 ratio salt, we first dissolved 26 mg (0.01 mol l⁻¹) into 20 ml of the salt stirring for over 20 hours, followed by adding 2.6 mg each by the same procedure as described above. We then stopped stirring to let the solution stand for over 3 hours, and visually checked the turbidity of the solution and precipitation. When no turbidity and no precipitation were observed, we again added 2.6 mg of the NiCl₂ powder and repeated the procedure until turbidity or precipitation was observed. We here defined the solubility of NiCl₂ as an integer of 0.001 mol l⁻¹.

**Electrochemical measurements.—** Working, counter, and reference electrodes were set and the electrolyte was poured into an inverted conical glass vessel and sealed to form a test cell. Test cells were placed on a heated plate to keep the temperature at 40 °C in the argon-filled glove box for cyclic voltammetry and other electrochemical measurements. CELL TEST-2 (Solastron) and potentio/galvanostat SP-200 (Bio-Logic) were used for the measurements.

**Surface analysis of the electrodes.—** Test electrodes were washed twice with acetonitrile dehydrated below 10 ppm (Kishida Chemical) and dried. The samples were offered with no exposure to air for analyses. XRD spectra of the surface of the electrodes were obtained by a D8 ADVANCE (BRUKER). The surface condition of the electrode was observed with a scanning electron microscope SU6600 (Hitachi). The product on the electrodes was identified with an X-ray photoelectron spectroscopy PHI Quanter SXM (ULVAC-PHI). Etching depth of nickel electrode was referred to the etching rate of SiO₂ standard thin film.

**Results and Discussion**

One of the most significant issues for metal chloride electrodes is excessive dissolution in electrolytes, and the solubility critically depends on basicity of the salt electrolytes. We therefore broadly investigated the dependency of NiCl₂ solubility on the AlCl₃/BPC electrolytes. The solubility increased with a decrease in the AlCl₃/BPC ratio: 0.001mol l⁻¹ for the 1.5/1.0 salt, 0.003 mol l⁻¹ for the 1.0/1.0 salt, and 0.015 mol l⁻¹ for the 0.9/1.0 salt. The formation of [NiCl₄]²⁻ ions may dissolve NiCl₂ into an electrolyte with a smaller ratio of AlCl₃/BPC,16 as follows:

NiCl₂ + 2Cl⁻ → [NiCl₄]²⁻ + 2e⁻  

Figure 1 illustrates cyclic voltammograms (CV) for Ni plate as “Ni electrode A” in AlCl₃/BPC with different molar ratios at 40 °C. The potential range was 0.55 V vs. Al/Al³⁺ for the 0.8/1.0 salt (Fig. 1a), 0.64 V vs Al/Al³⁺ for the 0.9/1.0 salt (Fig. 1b), and 0.22 V vs Al/Al³⁺ for the 1.0/1.0 salt (Fig. 1c), respectively. The scanning started in cathodic direction. The behavior in basic and acidic salts is very different because of variations in the nickel complex in the two regions. For the 0.8/1.0 and 0.9/1.0 molar ratio salts (Figs. 1a and 1b), Anodic current peaked at around 1.1–1.2 V vs. Al/Al³⁺, and the peak shifted positively with an increase in AlCl₃ ratio and through cycling. Considering the CV results in Ref. 23 and the fact that the solution turned blue after the measurement, the anodic peak may correspond to a reaction whereby Ni was oxidized and [NiCl₄]²⁻ ions produced, as follows:

Ni + 4Cl⁻ → [NiCl₄]²⁻ + 2e⁻  

On the other hand, weak cathodic current peak was observed at around 0.2–0.3 V vs. Al/Al³⁺. The cathodic peak may be due to the reduction of nickel oxides or Ni²⁺ ions;28,29 although it may contain complicated reduced products from nickel complex ions. This suggests that Reaction 2 progressed irreversibly or dominantly in the forward direction to form [NiCl₄]²⁻ ions.

For neutral-like AlCl₃/BPC salt with a molar ratio of 1.0/1.0, CV profiles are observed to differ from those of the basic salts (Fig. 1c). Prominent anodic peaks appeared at 0.4 and 0.5 V vs Al/Al³⁺ and the peak at around 1.1 V disappeared. This is thought to be the main reason why the EMF value of each electrode changed with the change in molar ratio of the AlCl₃/BPC salt15 and the change in EMF varies according to each electrode material.15,18 Anodic current in Fig. 1c was smaller than that in Figs. 1a and 1b. It suggests that difference in Cl⁻ ion concentration in the salts mainly caused the difference in anodic current.15 However, other factors as well as Cl⁻ ion concentration may affect to the difference in current, especially in near 1.0/1.0 molar ratio. Further study is needed to clarify it. The weak peak at around 0.15 V vs Al/Al³⁺ may be attributed to Ni deposition.28,29 In the region of more positive potential than 0.8 V vs Al/Al³⁺ in Fig. 1c, continuous current was observed through anodic and cathodic sweeps, which suggests that nickel continuously dissolved in the salt and a kind of ionic balance between [NiCl₄]²⁻, [NiCl₄]⁻, Ni²⁺, and other ions occurred to take the place of weak current peaks. In fact, the solution turned blue after the CV measurements, which suggests that

Figure 1. Cyclic voltammograms of Ni plate for the cell having Al coil as counter and reference electrodes and the AlCl3/BPC molten salt at 40°C. Scan rate was 1 mV s⁻¹. (a) AlCl3/BPC salt with molar ratio of 0.8/1.0. (b) AlCl3/BPC salt with molar ratio of 0.9/1.0. (c) AlCl3/BPC salt with molar ratio of 1.0/1.0.

Figure 2. XRD pattern of Al plate for the cell having Ni composite as positive, Al plate as negative electrode after standing for 16 hr at 40°C. (a) In AlCl3/BPC salt with molar ratio of 0.8/1.0. (b) In AlCl3/BPC salt with molar ratio of 1.5/1.0.

[NiCl₄]²⁻ ions formed in the salt and is related to the appearance of the weak current peaks. Further study is needed to clarify this point.

We confirmed [NiCl₄]²⁻ formation in the salts as follows: we assembled cells containing “Ni electrode B” as positive and “Al electrode B” as negative electrodes set at intervals of 15 mm into salt with AlCl₃/BPC molar ratios of 0.8/1.0 and 1.5/1.0. Two cells were placed under an open circuit for 16 hours at 40°C. The 0.8/1.0 molar ratio salt turned blue, but the 1.5/1.0 molar ratio salt did not change in color. We then washed the Al plate electrodes with acetonitrile in order to subject them to XRD and XPS measurements.

No peaks attributed to nickel were observed in the XRD pattern of the Al electrode in either of the two salts, as shown in Fig. 2a and Fig. 2b. On the other hand, Ni 2p and Al 2s XPS spectra indicated differences in the Al plate surfaces between the two salts. Nickel was not deposited, however, aluminum oxide film only existed on the Al surface for the 0.8/1.0 molar ratio salt (Fig. 3a). For the 1.5/1.0 molar ratio salt, however, more than 80 nm-thick Ni was deposited on the Al surface (Fig. 3b). This suggests that nickel oxides on the surface of nickel particles were dissolved and changed to stable [NiCl₄]²⁻ ions with excess Cl⁻ ions in the 0.8/1.0 molar ratio salt, and in the 1.5/1.0 molar ratio salt, nickel oxides were dissolved and deposited on the Al surface, replacing Al dissolution as a local cell reaction on the Al negative electrodes.

We then performed cyclic voltammetry for the slightly acidic, 1.05/1.0 molar ratio salt on the cell with Ni plate as a working electrode and Al coil as a counter and a reference. The rest potential was 0.92 V vs Al/Al³⁺ and the CV was started to scan in the cathodic direction. The result is shown in Fig. 4. A strong anodic peak was observed at 1.17 V vs. Al/Al³⁺ in the first sweep and weakly broad cathodic peaks were observed at around 0.5 and 0.2 V vs. Al/Al³⁺ in the second and later sweeps. The peak at 1.17 V vs. Al/Al³⁺ may be attributed to the nickel oxides, which were dissolved as [NiCl₆]⁴⁻ ions, and the weak broad cathodic peaks at around 0.5 and 0.2 V vs. Al/Al³⁺ are attributed to Ni plating and under potential deposition of Al.
On the surface of Al
At 15 nm depth

On the surface of Al
At 15 nm depth

At 80 nm depth

At 80 nm depth

Figure 3. Ni2p and Al2s XPS spectra of Al plate for the cell having Ni composite as positive, Al plate as negative electrode after standing for 16hr at 40°C. (a) In AlCl3/BPC salt with molar ratio of 0.8/1.0. (b) In AlCl3/BPC salt with molar ratio of 1.5/1.0.

Figure 4. Cyclic voltammograms of Ni plate for the cell having Al coil as counter and reference electrodes and the AlCl3/BPC molten salt with molar ratio of 1.05/1.0 at 40°C. Scan rate was 1 mV s⁻¹.

Figure 5. Ni2p XPS spectra of Ni plate after stopping cyclic voltammetry at the second anodic sweep at 0.95 V vs. Al/Al³⁺ at 40°C, followed by keeping the voltage for 12hr for the cell having Al coil as counter and reference electrodes and the AlCl3/BPC molten salt with molar ratio of 1.05/1.0.

Figure 6. Cyclic voltammograms of Ni plate for the cell having Al as counter and reference electrodes and the AlCl3/BPC molten salt with molar ratio of 1.1/1.0 at 40°C. Scan rate was 0.2 mV s⁻¹.

at 0.95 V vs. Al/Al³⁺, followed by oxidation of the Ni electrode at a constant voltage of 0.95 V vs. Al/Al³⁺ for 12 hours. We then washed the electrode with acetonitrile and dried it for XPS measurement. Figure 5 shows Ni2p XPS spectra for the surface and two different depths of the Ni electrode. Peaks attributed to NiCl₂ are observed at all depths. On the other hand, peaks attributed to Ni metal appeared by etching. This shows that 10 nm or thicker NiCl₂ layers formed on the Ni electrode: the anodic peak at 0.95 V vs. Al/Al³⁺ in the second and third sweeps of CV is attributed to the oxidation of Ni into NiCl₂.

We then performed the cyclic voltammetry for more acidic 1.1/1.0 molar ratio salts. The rest potential was 0.88 V vs Al/Al³⁺ and the CV was started to scan in the cathodic direction. In this case, the anodic current increased significantly (Fig. 6). Ni2p XPS spectra for the Ni electrode after three sweeps of cyclic voltammetry and after 12 hours of oxidation at a constant voltage of 1.0 V vs. Al/Al³⁺ are shown in Figs. 7 and 8, respectively. Both of Figs. 7 and 8 indicated the formation of nickel chloride on the electrode certainly. SEM photos of the surface of Ni electrodes before and after one and three sweeps of cyclic voltammetry are shown in Fig. 9. We observed that particulate
NiCl$_2$ had formed on the electrode after the third sweep of cyclic voltammetry. As for the reason why the peak at 1.0 V vs. Al/Al$^{3+}$ in the first anodic sweep did not appear (Fig. 6), it was supposed that the surface area of the Ni plate electrode was not large enough to produce NiCl$_2$ on the electrode. The peak appeared and became large because the Ni plate roughened through repeating sweep. In fact, it was observed that the first anodic sweep changed the surface state of Ni plate electrode as Ni dissolved to nickel ions as shown in Figs. 9a and 9b. Figure 10 illustrates typical results of EDX analysis for the deposited layer on the Ni electrode surface after the third sweep of cyclic voltammetry for the 1.05/1.0 molar ratio salt. The results show Ni and Cl exist uniformly on the Ni electrode surface, which suggests that nickel oxidized to produce NiCl$_2$ on the electrode.

We then demonstrated the formation of NiCl$_2$ by oxidation of Ni in acidic AlCl$_3$/BPC with molar ratios of 1.05/1.0 and 1.1/1.0 through XPS measurements. XPS measurement is effective for analyzing NiCl$_2$ as an oxidation product of Ni, but etching with Ar gas occasionally reduces the metal chlorides (for example FeCl$_2$, MnCl$_2$), and the energy peaks of the metal chloride are close to those of the corresponding metal, which interferes identification of the reaction products. We thus also tried to identify the NiCl$_2$ using XRD as a measurement that can avoid such defects.

We performed cyclic voltammetry for a cell containing 0.1 mm-thick, 12 mm-wide and 15 mm-long Ni plate as a working electrode, Al coil as a counter and a reference and AlCl$_3$/BPC electrolyte with...
a molar ratio of 1.1/1.0 once, starting in the cathodic direction, and stopped the second anodic sweep at 1.0 V vs. Al/Al$^{3+}$ at 40 $^\circ$C, followed by 24 hours of oxidation at a constant voltage of 1.0 V vs. Al/Al$^{3+}$ to produce NiCl$_2$ on the electrode. Then we measured the NiCl$_2$ film formed on the surface of the Ni electrode by low-incidence XRD (the incidence angle was fixed at 3 $^\circ$ and the instrument was operated in a step-scan mode in increments of 0.02$^\circ$ with counts accumulated for 1.5 s at each step). The XRD pattern of the Ni electrode is shown in Fig. 11. The data indicate the existence of a thin NiCl$_2$ film on the Ni surface.

We estimated the electrochemical properties of the Ni electrode in more acidic AlCl$_3$/BPC salt with a molar ratio of 1.5/1.0. We further performed cyclic voltammetry at a scan rate of 0.2 mV s$^{-1}$ at 40 $^\circ$C, and 12 hours oxidation at 1.0 V vs. Al/Al$^{3+}$ after stopping the second anodic scan of the CV at 1.0 V vs. Al/Al$^{3+}$. The results are shown in Figs. 12 and 13. The rest potential was 0.87 V vs Al/Al$^{3+}$ and the CV was started in the cathodic direction. An anodic peak at around 1.0 V vs. Al/Al$^{3+}$ appeared in the second and third sweeps. This indicates NiCl$_2$ formation on the surface of Ni, and the feature is the same as that for other acidic salts. However, the Ni$^{2+}$ XPS spectra suggested less NiCl$_2$ formation than for other acidic salts.

Regarding our results, NiCl$_2$ formation by oxidation of Ni occurs under conditions of limited acidity in AlCl$_3$/BPC. Nickel is oxidized into [NiCl$_4$]$^{2-}$ in basic and neutral AlCl$_3$/BPC salts where the majority of Cl$^-$ ions exist. In the AlCl$_3$/BPC with molar ratios of 1.05/1.0 and 1.1/1.0 where limited Cl$^-$ ions exist, it appears that the nickel is oxidized to nickel chloride with chloride ions formed through reduction of the [AlCl$_4$]$^{-}$ or [Al$_2$Cl$_7$]$^{-}$ ions at the negative electrode, because the slightly acidic conditions mainly contain [AlCl$_4$]$^{-}$ and [Al$_2$Cl$_7$]$^{-}$ ions.

This NiCl$_2$ formation, however, decreased in more acidic AlCl$_3$/BPC with the AlCl$_3$ ratio larger than 1.1. It is considered that Ni is dissolved to form [Ni(Al$_2$Cl$_7$)$_3$]$^+$ and [Ni(Al$_2$Cl$_7$)$_3$]$^{2+}$ ions, because [Al$_2$Cl$_7$]$^{-}$ ions may exist predominantly in the strong acidic conditions at a molar ratio of 1.5/1.0. We therefore observed the linear increased in anodic current with shifted potential positively from 1.0 V vs. Al/Al$^{3+}$ only in the 1.5/1.0 molar ratio salt (Fig. 12). Further study is also needed to clarify the reaction mechanism.

Summary

We studied the electrochemical properties of nickel in molten salt containing AlCl$_3$ and 1-butylpyridinium chloride (BPC) at 40 $^\circ$C. We mainly performed cyclic voltammetry to investigate the reaction and XPS and XRD to identify the reaction products. The results we obtained are summarized as follows:

(1) Solubility of the reaction product into the electrolyte critically affects the efficiency of the electrochemical reaction. Our approximation of NiCl$_2$ solubility showed a 15-fold difference between AlCl$_3$/BPC molar ratios of 1.5/1.0 and 0.9/1.0.

(2) Regarding the results of cyclic voltammetry of nickel, nickel was oxidized to produce NiCl$_2$ in slightly acidic AlCl$_3$/BPC salts with molar ratios of 1.05/1.0 and 1.1/1.0. The NiCl$_2$ produced in the acidic salt with a ratio of 1.5/1.0 was less than that produced in the slightly acidic 1.05/1.0 and 1.1/1.0 salts because of differences in the ionic species in the salt.

(3) XPS data suggested that no NiCl$_2$ was produced on the electrode in basic and neutral salts. In the salts, the electrolyte turned blue, which suggests that nickel was oxidized into [NiCl$_4$]$^{2-}$ ions.

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