FUNDAMENTAL STUDIES OF NICKEL ELECTRODE IN A BASIC Na[AlCl₄] MELT AT 300°C

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ABSTRACT

The electrochemistry of the Ni/NiCl₂ electrode reaction was studied using Al/Na[AlCl₄] -NaCl/NiCl₂/Ni cell in which the capacities of the cell were limited by the Ni/NiCl₂ electrode. The limiting mechanism of the electrode was found to be associated with the formation of NiCl₂ on the surface of the nickel electrode. This phenomenon limits the mass transfer processes of the non-porous electrode and thus its area capacity density. Modifying the electrolyte with the NaBr and NaI additives was found to produce higher nickel utilization and lower impedance values due to doping effects, which is believed to open up the lattice for better mass transport. The solubility measurements indicate that the solubility of nickel chloride in the chloroaluminate melt is strongly dependent on the operational temperature of the cell and the chemical additives present in the electrolyte. The corrosion studies suggest that the nickel chloride material in the positive electrode is in thermodynamic equilibrium with the metallic constituent and, as a result, does not appear to attack current collector materials made of the same metal.

INTRODUCTION

The sodium/nickel chloride cell couple is a very promising sodium/beta-alumina battery couple (1-7). The high theoretical specific energy (790 Wh/kg), high cell voltage (2.59 V), wide temperature range, cell failure mode, and good cycling characteristics of this battery systems have made it a viable candidate for electric vehicle propulsion. The Na/NiCl₂ cell is similar to the Na/S cell in that it uses much of the same technology. For instance, the Na/NiCl₂ cell, like the Na/S, uses a liquid sodium negative electrode and the β"-alumina solid electrolyte. However, unlike the sodium/sulfur cell, it uses a secondary electrolyte of molten sodium tetrachloroaluminate (Na[AlCl₄]) in the positive electrode and an insoluble nickel chloride as the active material. The Na[AlCl₄] electrolyte conducts sodium ions from the β"-Al₂O₃ electrolyte to the nickel chloride electrode reaction sites. The cell reaction is

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2\text{Na} + \text{NiCl}_2 = 2\text{NaCl} + \text{Ni}
\]

The specific power and energy of the present battery construction, however, is modest due to the performance-limiting positive electrode. The performance of the present Na/NiCl₂ batteries, despite their high theoretical specific energy and cell voltage

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is limited due to the performance-limiting characteristics of the positive electrode. The nickel chloride electrode thus plays an important role in the resistance and weight of the cell; consequently, a quantitative understanding of the chemical and electrochemical behavior of the NiCl₂ is very important. This paper describes the fundamental chemical and electrochemical properties of the Ni/NiCl₂ electrode to better understand the working mechanism, and the effect of conditions that influence the performance parameters of the electrode.

EXPERIMENTAL

Electrochemical Studies

Half-cell experiments were conducted to investigate the electrochemical properties of the Ni/NiCl₂ electrode in NaCl saturated Na[AlCl₄] melt. A surface-polished nickel wire electrode (0.33 cm²) was cycled galvanostatically against a large surface area (6-cm²) aluminum counter electrode. Because of the large area, the aluminum electrode shows negligible polarization and can be used as a reference electrode. The effect of chemical additives on the electrochemical behavior of the nickel chloride electrode was studied by incorporating 1.0 wt% NaF, NaBr, and NaI into the chloroaluminate melt.

Solubility Studies

For the solubility studies, molten Na[AlCl₄] was saturated with NiCl₂ at several temperatures between 200 and 450°C. In some cases, the NiCl₂-saturated equilibrated solution was generated in a Na / Na[AlCl₄], NaCl, NiCl₂ /Ni cell. For the nickel chloride solubility measurements the nickel chloride electrodes were cycled galvanostatically in the anodic (3.0 V) and cathodic (2.0 V) directions against the Na electrode simulating the potentials in the Na/NiCl₂ cell. The chloroaluminate composition is characterized by the AlCl₃/NaCl mole ratio. The mole percent of AlCl₃ was adjusted by additions of small measured quantities of AlCl₃ to the NaCl-saturated melt of known weight. Basic melts such as the electrolyte used in Na/NiCl₂ cells, was obtained at AlCl₃:NaCl (with NaCl greater than 1:1 ratio). The NaCl-saturated electrolyte had 49.75:51.25 (AlCl₃:NaCl) ratio. This value changes only slightly in the temperature range of interest (200-400°C). For analysis, about 1-g samples of the NiCl₂ saturated molten salt were removed from these cycled cells with a thermally equilibrated sample tube. The nickel content of the sample was determined by a spectrophotometric method from a chloroform extract of aqueous nickel-heptoxime solution.

Corrosion Studies

For corrosion tests, the nickel specimens were placed in an alumina crucible containing the chloroaluminate electrolyte, and then lowered in the high-temperature well in the He-atmosphere glove box. The specimens were analyzed for weight and thickness after selected time intervals. In some cases, the nickel specimens were removed from the cell assembly in the fully charged state. In-situ stress corrosion was investigated on nickel-200 and stainless steel-304 wires which were electrochemically cycled between 2.0 and 3.0 V vs. Na reference electrode and kept under tension (60 Mpa) in the molten...
electrolyte at 300°C. The wires were monitored for the development of intergranular corrosion, which was indicated by wire breakage.

RESULTS AND DISCUSSION

Electrochemistry of Ni/NiCl₂ Electrode

The Ni/NiCl₂ electrode was charged and discharged between 1400mV (charge) and 400 mV (discharge) against the aluminum electrode. This range is equivalent to 2.04 V and 3.04 V cell-voltage cut-off for a Na/NiCl₂ cell. It was observed that the Ni/NiCl₂ electrode capacity gradually improves in the first 8-10 cycles and then reaches a steady condition. Figure 1 shows the effect of temperature on area-capacity limits (ACL) as well as area-specific impedance (ASI₅) within the temperature range of 200-400°C, which is the practical operational temperature range of the Na/NiCl₂ cell. The effect of temperature is reflected in the observed ASI₅ and capacity densities, which were measured by 15 s current interruptions during galvanostatic cycling. It can be seen from this figure that the area capacity of nickel electrode increases initially when the temperature is increased from 200 to 225°C. Further increase in the temperature does not improve the area capacity. The initial increase in the area-capacity is thought to be due to the decreased impedance of the solid NiCl₂ layer at temperatures between 200 to 225°C. However, the high resistance of the NiCl₂ layer on the surface of the Ni electrode ultimately limits the thickness of the layer. These phenomena results in a limited area capacity of the nickel electrode even at higher temperatures and in the presence of a surplus of NaCl in the chloroaluminate melt.

A comparison of the area-capacity limit of the nickel electrode in the presence of chemical additives such as NaF, NaBr, and NaI is also shown in Figure 2. It can be seen from Figure 2 that the bromide and iodide additives produce the higher ACL compared to chloride. Fluoride produced the lowest ACL. In the case of iodide additive, the nickel electrode was charged at potential (1.20 V vs. Al) lower than the potential for iodine evolution (~ 2.89V vs. Na). From previous measurements without the additives, we know that only a certain limited capacity, the ACL (C/cm²), can be produced anodically on the surface of nickel, even when a surplus of NaCl is available in the chloroaluminate melt. The bromide and iodide ions help to develop a higher capacity, lower-impedance of the NiCl₂ electrode compared with an additive-free electrode system. The increase of ACL is significantly more than the charge equivalent of the addition of the chemical additives. The improvement in the area-capacity limit is thought to be due to the decreased impedance of the solid NiCl₂ layer in the presence of bromide and iodide ions. In addition, the doping of the nickel chloride layer may also modify the morphology of the layer due to increased lattice parameters for NiF₂ (a: 4.6508 Å, b: 3.0837 Å), NiCl₂ (a: 3.478Å, b: 17.41 Å), NiBr₂ (a: 3.723 Å, b: 18.34 Å), and NiI₂ (a: 3.929 Å, b: 19.817 Å). The increased lattice dimensions may help the ion transport during charge and the discharge processes.

The present experiments indicate that Ni/NiCl₂ cell couple forms a high resistance NiCl₂ layer on the surface of the Ni electrode when anodically produced. Although this layer may be porous at the beginning, it ultimately limits the thickness of the layer. This phenomenon sets an upper limit of the electrode area capacity and capacity loading.
density of the battery itself. Nevertheless, the same phenomenon permits one to use nickel as a current collector without the need for an additional, "inert" current collector material.

The working hypothesis of an insulating surface layer gives insight to the fabrication of high-performance Ni electrodes. Because the electron pathway is exclusively in the metallic nickel, thus the nickel structure must be continuous. The sintering process must also provide a microstructure of high inner surface area with cavities bigger than about 20-50 \( \mu \text{m} \). This cavity size is required to provide liquid electrolyte channels within the pores even when solid NaCl forms during the discharge. The NaCl deposits observed in the Na/NiCl\(_2\) range in size from 20-50 \( \mu \text{m} \) \((8)\). The required inner-surface area can be calculated on the basis of the measured area capacity values, which are in the range of 0.1-1.5 \( \text{C/cm}^2 \) depending on the conditions. In addition to the macro-pore structure one must produce a micro-pore structure on the inner surface of the Ni electrode. This micro-pore structure would represent the high surface area found in the broken-in electrode of the present experiment and would significantly enhance the capacity without the lengthy break-in period.

**Nickel Chloride Solubility**

To better understand the lifetime-limiting factors of the Na/NiCl\(_2\) cell, the solubility and interaction of NiCl\(_2\) in the chloroaluminate melt is of critical importance. The dissolved NiCl\(_2\) certainly interacts with the chloroaluminate system and the \( \beta''\)-alumina tube itself in a Na/NiCl\(_2\) cell. A high concentration of the Ni\(^{2+}\) ions in the chloroaluminate melt could exchange with the Na\(^+\) ions of the \( \beta''\)-alumina, resulting in lowered conductivity and stability of this component of the Na/NiCl\(_2\) cell. Thus, the exchange would jeopardize the \( \beta''\)-alumina integrity and reduce the cell life. The reactions taking place in the basic melts can be compared with the chemistry of Fe-Co-Ni family of elements. Although the concentration of the dissolved nickel chloride may be low, it is still important to consider the adverse effect of the Ni-species on the stability of the beta-alumina. This effect may be caused by Ni\(^{2+}/\text{Na}^+\) ion exchange and subsequent Ni\(^{2+}\)-ion migration in the solid electrolyte. The form of the dissolved Ni species makes a very important difference to the extent of ion exchange and possible damage to the \( \beta''\)-alumina.

Figure 3 shows the observed solubility of NiCl\(_2\) in NaCl-saturated Na[AlCl\(_4\)] melt as a function of temperature. Although the solubility is low below 300°C, it rapidly increases with temperature. At low temperatures (< 250°C) the saturated solution is almost colorless, but an ultramarine-blue color of greater and greater intensity develops as the temperature is increased. At 400°C, the solution resembles blue ink. The blue color is attributed to the [NiCl\(_4\)]\(^2-\) complex anion, which appears to be stable in the NaCl-saturated (basic) chloroaluminate melt. At 450°C, about 2500 ppm nickel as NiCl\(_2\) was detected in the melt. It is clear from this figure that the solubility of NiCl\(_2\) increases significantly with increasing temperature. The solubility increases more than an order of magnitude in NaCl-saturated molten Na[AlCl\(_4\)] when the temperature is increased from 200 to 360°C. The acid/base equilibrium of the chloroaluminate melt \((9)\) interacts with a complex formation of the nickel species. In NaCl-saturated basic melts, nickel is present mainly as a complex ion, according to the reaction \(2\).
The higher saturation concentration of NaCl in Na[AlCl₄] at increasingly higher temperature (10), although promotes dissolution of NiCl₂, actually decreases the ion-fraction of the simple ion from [Ni²⁺] by stabilizing nickel in the [NiCl₄]²⁻ form according to the above reaction. This reaction, if the basicity of the melt is maintained, stabilizes nickel in the [NiCl₄]²⁻ ion form and reduces the concentration of the Ni²⁺. This, in turn, significantly reduces the ion-exchange between nickel and sodium in the β”-alumina tube due to size effect. This fact clearly underlines the importance of maintaining basic electrolyte. A buffered basic melt can be maintained by having an excess solid NaCl in the Ni electrode at all times. Solid NaCl is also needed to compensate for the effect of the charge reaction, which may produce local acidity in the nickel electrode, especially at high current densities.

In Figure 4, the saturation concentrations of the nickel species are compared for NaCl-saturated melts with and without additives. The sulfur additive is typically used in the practical Na/NiCl₂ batteries to control the morphology of the Ni/NiCl₂ electrode and stabilize cell capacity (1-5, 6, 8). As Figure 4 shows that sulfur additive alone can reduce the solubility of NiCl₂ in NaCl-saturated Na[AlCl₄] melt. The combination of the sodium bromide, sodium iodide, and sulfur additives significantly reduces the solubility even further, down to the ppm level. The NaCl-saturated melt containing the chemical additives probably stabilizes the nickel in the complex-ion form and, thus, very effectively hinders the ion exchange in the β”-alumina electrolyte and extends the cycle life. Also, to lower the nickel concentration even more, low temperature operation of the cell is desirable. By systematic application of these principles to cell design, one can improve the specific energy and extend the cycle life of the Na/NiCl₂ battery.

Nickel Corrosion

Figure 5 represents weight and thickness changes vs. time data obtained for chemical and electrochemical dissolution of the Ni-200 specimens at 300°C. The initial increase in the thickness and weight loss reflects the initial charging reaction of the nickel metal. From the results of corrosion weight and thickness loss tests, the corrosion behavior of the nickel in chloroaluminate melt can be divided into two regions: first, where the corrosion rate increases with increasing test time, and, second, where the corrosion rate does not increase but remains constant with time. First region corresponds to the initial oxidation of nickel metal to nickel chloride, and the second region corresponds to the achievement of the area-capacity limit as shown in Figure 1. Results of the stress corrosion tests on type 304 stainless steel and Ni-200 wires during electrochemical cycling and under tension (60 MPa) in NaAlCl₄ melt containing 2 wt% S at 300°C are shown in Figure 6. These, investigations were conducted under the battery cycling regimes. After 1400 hours of exposure of the Ni-200 wires, no signs of stress corrosion were observed whereas the stainless steel wire failed within few hours at UTS in the range of 40-100%.

These experiments also suggest that the electrically low conducting nickel chloride layer formed on the surface of the nickel metal prevents further thickening of the layer and thereby limiting the charge uptake and, consequently, the further corrosion. This phenomenon sets an upper limit of the nickel chloride layer thickness and hence self-
protection mechanism for nickel against corrosion. It seems reasonable that the high degree of inhibition is achieved by the formation of the nickel chloride barrier layer. This phenomena is advantageous from the aspect of permitting the use of the nickel structures as the current collector and cell-case assembly in the ZRBRA cells.

CONCLUSIONS

The basic mechanism of the Ni/NiCl₂ electrode operation in chloroaluminate was identified as a high resistance nickel chloride layer formation on the surface of the Ni electrode. The area-capacity limit is in the range of 0.1-1.5 C/cm² depending on the current density and operating temperature. The chemical additives significantly enhanced the nickel utilization due to modified surface layer and enhanced lattice parameters. The solubility measurements show that the solubility of nickel chloride in the chloroaluminate melts is strongly dependent on the temperature, melt composition, and the chemical additives present in the electrolyte. Solubility of NiCl₂ increases about two orders of magnitude in NaCl-saturated molten Na[AlCl₄], from 15 to 1500 ppm as nickel, when the temperature is increased from 200 to 400°C, with the major part of this increase occurs above 340°C. Three main factors that reduce the Ni²⁺ concentration in the chloroaluminate melt are low operational temperature of the cell, the basicity of the melt, and the use of chemical additives. These findings provide the logical basis for designing effective electrode structures for high performance Na/NiCl₂ batteries with long cycle-life. An important feature of the Na/NiCl₂ cell is that the nickel chloride material in the positive electrode is in thermodynamic equilibrium with the metallic constituent and, as a result, does not appear to attack current collector materials made of the same metal. Thus, it is possible to fabricate both the current collectors and the cell container of these relatively inexpensive and easily welded materials without the expense of applying a corrosion resistant coating. The results of these investigations show that Ni-200 is suitable for use in the ZEBRA cells both as current collector and cell container.

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Figure 1. Limiting area capacity and area-specific impedance of a nonporous nickel electrode in NaCl-saturated Na[AlCl₄] melt.

Figure 2. Area capacity limits of Ni/NiCl₂ electrode in NaCl-saturated Na[AlCl₄] electrolyte containing chemical additives.
Figure 3. Solubility of NiCl$_2$ in NaCl-saturated Na[AlCl$_4$] melts as function of temperature.

Figure 4. Solubility of NiCl$_2$ in NaCl-saturated Na[AlCl$_4$] melt as function of temperature in the presence and absence of chemical additives.
Figure 5. Weight and thickness changes of the nickel current collector during electrochemical cycling in chlorolaluminate melts with no additives and in chlorolaluminate melts containing 10-wt% NaI, 5 wt% NaBr, and 2 wt% sulfur additives at 300°C.

Figure 6. In-situ stress corrosion of Ni-200 and stainless steel-304 wires at 300°C during electrochemical cycling and under tension (60 Mpa).