Electrochemistry of Nonporous $Ni/NiCl_2$ Electrode in Chloroaluminate Melt

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The sodium/nickel chloride cell couple is a very promising sodium/beta-alumina battery couple (1-4). 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 $Na/NiCl_2$ cell is similar to the Na/S cell in that it uses much of the same technology. For instance, the $Na/NiCl_2$ 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 ($Na[AlCl_4]$) in the positive electrode and a nickel chloride as the active material. The $Na[AlCl_4]$ electrolyte conducts sodium ions from the β"-Al_2O_3 electrolyte to the nickel chloride electrode reaction sites. The cell reaction is

$$2Na + NiCl_2 = 2NaCl + Ni$$

Electrochemical Behavior of the positive electrode $Ni/NiCl_2$ in the $Na/NiCl_2$ cell was studied using Al/ $Na[AlCl_4]$ -NaCl/$NiCl_2$/Ni cell in which the capacities of the cell were limited by the $Ni/NiCl_2$ electrode. The limiting mechanism of the electrode is associated with the formation of $NiCl_2$ 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. In addition, the nickel chloride film on the positive electrode is in thermodynamic equilibrium with the metallic constituent and, as a result, does not 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. Modifying the electrolyte with the NaBr, NaI and sulfur additives was found to produce higher nickel utilization due to doping effects which is believed to open up the lattice for better mass transport. Solubility of the nickel chloride in sodium-chloroaluminate melts as function of temperature and additives were also determined. The solubility measurements indicated that the solubility of nickel chloride in the chloroaluminate melt is strongly dependent on the operational temperature of the cell and the acidity-basicity of the electrolyte. The acid/base equilibrium of the chloroaluminate melt (5) 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 following reaction.

$$[NiCl_4]^{2-} + 4AlCl_3 = 2[Al_2Cl_7]^- + Ni^{2+} + 2Cl^-$$

The higher saturation concentration of NaCl in $Na[AlCl_4]$ at increasingly higher temperature (6), although promotes dissolution of $NiCl_2$, actually decreases the ion-fraction of the simple ion from $[Ni^{2+}]$ by stabilizing nickel in the $[NiCl_4]^{2-}$ form according to the above reaction. This reaction, if the basicity of the melt is maintained, stabilizes nickel in the $[NiCl_4]^{2-}$ ion form and reduces the concentration of the Ni^{2+}. 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. The effect of the chemical additives, basicity of the melt, and the cell operating temperature on the $Na/NiCl_2$ cell performance will be discussed in the meeting.

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