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HIGH-TEMPERATURE SODIUM NICKEL CHLORIDE BATTERY FOR ELECTRIC VEHICLES

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ABSTRACT

Although the sodium/nickel chloride cell couple has a high voltage (2.59 V) and a high specific energy (790 Wh/kg), the performance of present incarnations of this battery tend to be limited by their power. Because the nickel chloride electrode dominates the resistance and weight of the cell, research on this cell couple at Argonne National Laboratory (ANL) has been primarily directed toward improving both the specific power and energy of the NiCl₂ electrodes. During the course of these investigations a major breakthrough was achieved in lowering the impedance and increasing the usable capacity through the use of chemical additives and a tailored electrode morphology. This improved Ni/NiCl₂ electrode has excellent performance characteristics, wide-temperature operation and fast recharge capability. Modeling studies done on this electrode indicate that a fully developed Na/NiCl₂ battery based on ANL-single tube and bipolar designs would surpass the mid-term and approach the long-term goals of the U.S. Advanced Battery Consortium.

INTRODUCTION

To reduce U.S. dependence on petroleum-based fuels and alleviate environmental problems in urban areas, advanced high-performance batteries for electric vehicle (EV) propulsion are being developed. Batteries designed for EV propulsion must satisfy several demanding requirements. The most important technical requirements assigned by the U.S. Advanced Battery Consortium (USABC) are the mid-term and long-term goals for high specific energy (100 and 200 Wh/kg), respectively and peak power (200 and 400 W/kg), respectively. The sodium/nickel chloride cell system, owing to its excellent properties such as high theoretical energy, safety, and good cycling characteristics, is one of the best candidates for EV applications among several battery systems under development. Currently, the test cars equipped with Na/NiCl₂ batteries are being manufactured and very successfully tested in Europe.
The Na/NiCl₂ cell uses a liquid sodium electrode and the β⁺-alumina solid electrolyte. It uses a secondary electrolyte of molten sodium tetrachloroaluminate (NaAlCl₄) in the positive electrode and the insoluble nickel chloride as the active material. The NaAlCl₄ electrolyte serves to conduct sodium ions from the β⁺-alumina electrolyte to the nickel electrode reaction.

The cell diagram of the Na/NiCl₂ cell is

\[
- \text{Ni/Na/β⁺-alumina/Na[AlCl₄], NaCl/NiCl₂/Ni} +
\]

Sodium and Na[AlCl₄] are molten at the operating temperature (250-300°C) of the cell. Na[AlCl₄] is added to the porous Ni/NiCl₂ electrode to transport Na⁺ ions from the surface of the β⁺-alumina electrolyte to the reaction sites at the interior of the positive electrode. The cell reaction is

\[
2\text{Na} + \text{NiCl₂} = 2\text{NaCl} + \text{Ni}
\]

FUNDAMENTAL STUDIES OF Ni/NiCl₂ ELECTRODE

Several basic studies were carried out on the nickel chloride electrode. The purpose of these investigations was to better understand the charge and discharge processes, and then to find ways to improve the performance of the Ni/NiCl₂ electrode. Investigations [1-4] were carried out on nonporous and porous electrodes by using a variety of techniques such as potentiometric, coulometric, cyclic voltammetry, porosimetry, and BET area measurements. The results suggested that the low-conducting nickel chloride layer formed on the nickel electrode matrix tended to limit both the utilization and power of the electrode. The increasing resistance of the charge product stopped the further thickening of the layer and thereby limited the charge uptake and, consequently, the available capacity in the subsequent discharge. We termed this available capacity the "area-capacity limit" (ACL). Depending on the conditions, e.g., temperature, the ACL is 0.4-0.8 C/cm² of the true surface area of the nonporous nickel electrode. During discharge, on the other hand, the NaCl formation (Eq. 2), accompanied by increasing impedance, limited power. The effects of pore-size distribution on electrode performance was investigated by measuring capacities of model electrodes of various porosities (nonporous Ni, Ni felt, Ni powder sintered with and without poreformer) under identical conditions. From the results, we determined the optimum pore-size distribution of the nickel electrode. Results also indicated that capacity density (mAh/cm³) improved with increased BET surface area [5]. These measurements provided a firm theoretical basis for the improvement of the modified-morphology Ni/NiCl₂ electrodes whose performance is shown in Fig. 1. These earlier studies also suggested that a porous electrode with a specially tailored morphology would improve performance by providing high surface area and sufficient pore cavities to support effective mass transport. Also, we
found indications with these experiments that chemical additives would improve the properties of the electrochemically forming NiCl₂ layer.

PERFORMANCE CHARACTERIZATION OF Na/NiCl₂ LABORATORY CELLS

Performance characterization of the Ni/NiCl₂ electrodes in terms of the energy density and area-specific impedance was carried out in small Na/NiCl₂ research cells of about 0.6-1.8 Ah capacity. The research cell models the components and mimics the operational conditions of a full-size Na/NiCl₂ cell. By providing one-dimensional current density distribution in the Ni/NiCl₂ electrode, we can precisely measure the important electrochemical engineering parameters [6] necessary for the modeling and performance-projecting calculations that we use to evaluate designs of full-size batteries.

In an effort to reduce the resistivity of the nickel chloride layer, the chemical additives sodium bromide and sodium iodide were incorporated into the electrode. The morphology of the sintered nickel chloride electrode was modified by using a poreformer to attain controlled pore-size distribution. We found that a combination of the chemical additives (NaBr, NaI, and sulfur) in the modified morphology electrode has a significant synergistic effect, producing a nickel chloride electrode with excellent capacity and very low impedance [4]. The chemical additives produce high nickel utilization and low electrode impedance, probably due to doping effects. By identifying an optimal combination of additives, we were able to increase the utilization of the nickel matrix from 15% to about 45%. Figure 1 shows the area-specific impedance (ASI₁₅₀), measured by an interrupted galvanostatic method, as a function of discharged capacity per unit volume for baseline and improved Ni/NiCl₂ electrodes. The termination points of the curves at progressively higher utilized capacities indicate increased available energy density (Wh/cm³), and the lowered area-specific impedance of the Ni/NiCl₂ electrode (ohm. cm) indicates higher power capability. The ASI of the Ni/NiCl₂ electrode was calculated by subtracting the ASI of the Na/β'₅-alumina electrode, which was measured in separate experiments, from the cell value. This improved electrode can also be rapidly recharged at a 1C rate with good discharge capacity (Fig. 2).

The effect of temperature on the performance was also investigated in these small research cells. It was observed that increased temperature improves energy density and lowers the impedance for the Na/NiCl₂ cell. The trend leads us to expect more improvement at even higher temperatures, but, because of the higher solubility of the nickel species, this performance-improving approach has questionable value. Earlier Ni/NiCl₂ electrodes had to be operated at 300°C or higher to achieve acceptable performance (Fig. 3). Our latest Ni/NiCl₂ electrode composition (ANL 92), however, can be operated with acceptable performance in Na/NiCl₂ cells even at 150°C (Fig. 3). The exceptionally wide operating temperature range (150-400°C) permits easy thermal management solutions.
SEALED Na/NiCl₂ CELLS INVESTIGATIONS

The ANL technology was transferred to Eagle-Picher Industries who made sealed cells. The primary goal of these collaborations was to demonstrate the viability of ANL technology in sealed cells and establish quantitative relationships between performance data measured in the laboratory-scale cells and sealed cells. The cells did not show any sign of major capacity degradation. One of the cells with inside cathode geometry was tested for more than 1000 cycles, including several overcharge and overdischarge cycles as well as freeze-thaw cycles. The overall performance of these cells was similar to that found in the lab-scale cells (see Fig. 4 and Fig. 5). The decomposition voltage of one of the additives, NaI [7], however, is within the operating voltage range of Na/NiCl₂ cell. Therefore, we have also investigated whether iodine gas evolution would cause excessive pressure in a sealed Na/NiCl₂ cell and what role it plays in the Ni/NiCl₂ electrode processes [8]. To measure the pressure inside the positive electrode compartment, a special high-temperature pressure gauge was developed. The pressure gauge was attached to the positive electrode compartment via a nickel tube and operated isothermally with respect to the cell, thereby avoiding any condensation in the pressure-sensing bellows. In the whole-cell operating conditions, the pressure inside the cell in the absence of iodine evolution agreed with the laws of thermal expansion of gases. Only a small additional pressure increase (1-2 kPa) was observed in the critical iodine-producing voltage range (above 2.8 V under normal cell cycling conditions).

MODELING PERFORMANCE PROJECTIONS OF Na/NiCl₂ BATTERY

A modeling procedure, that uses the measured area-specific impedance data as input has been developed [9]. This particular modeling procedure is very useful to evaluate various full-size cell and battery designs to determine which configuration would meet EV performance requirements and also provide good fabricability [10]. Designs for batteries of single-tube-cell, multiple-tube-cell, and bipolar constructions have been devised and analyzed for performance. The projected energy and power values for batteries built with single-tube (β"-alumina) and bipolar cells indicate (Fig. 6) that a fully developed Na/NiCl₂ battery based on ANL single-tube and bipolar designs would surpass the mid-term and approach the long-term goals of the USABC.

SUMMARY

We have demonstrated that the use of chemical additives and controlled morphology has substantially improved the performance of Na/NiCl₂ cells. A fully developed Na/NiCl₂ battery based on ANL’s improved chemistry and morphology and design concepts would surpass the mid-term requirements of the USABC for EV propulsion, and the performance of a bipolar construction could approach the long-term goals of the USABC.
In addition, we have also demonstrated that the improved ANL Na/NiCl₂ battery system can offer numerous advantages. First is its exceptionally wide and safe operational temperature range, 150-400°C, which is the most advantageous temperature range for dynamic high-power applications such as electric cars. No other battery system has such a temperature range. This range, spanning 250°C, would make battery construction simple and inexpensive because the need for peripheral components such as a narrow-range temperature control is minimized. Second, in this battery, three times more energy per weight of nickel can be stored than in the other nickel battery systems under development. The Ni/Cd, Ni/metal hydride, Ni/H₂, Ni/Zn, and Ni/Fe cells require about 6.3 kg nickel/kWh; in contrast, the Na/NiCl₂ cell requires less than 2 kg nickel/kWh. (These numbers include the weight of nickel in the electrodes, current collector, and other cell hardware). This advantage arises from the high cell voltage (2.6 V) and the new electrode. Third, no gases evolve even during abusive conditions. Therefore, the cells can be hermetically sealed. Because of the sealed construction and easy recycling of used batteries, this system is environmentally safe.

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REFERENCES


4. US Patent 5,283,135


Fig. 1. Performance characteristics of 0.5-cm thick Ni/NiCl₂ electrodes at 300°C.
Fig. 2. Effect of current density and recharge time on discharge energy.
Fig. 3. Effect of temperature on discharge capacity of a 0.5-cm thick ANL 92 Ni/NiCl₂ electrode; 20 mA/cm current density.
Fig. 4. Effect of chemical additives in sealed Eagle-Picher cells.
Fig. 5. Power/Energy characteristics of sealed Eagle-Picher cells.
Fig. 6. Performance projections of ANL Na/NiCl₂ battery.