

Short Communication

Alkaline nickel/tin cell system

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Abstract

A secondary nickel/tin alkaline cell of 1 A h capacity has been assembled and subjected to charge/discharge studies at different rates. The discharge data were fitted to the general discharge equation of a secondary cell in order to determine the reversibility of the system. The cell's characteristics and limitations are discussed.

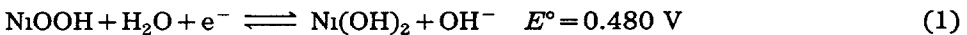
Introduction

Of the various alkaline nickel batteries, nickel/tin (Ni/Sn) is a novel system expected to possess fairly good performance characteristics in addition to a reasonably high cycle life. The cell system is represented by

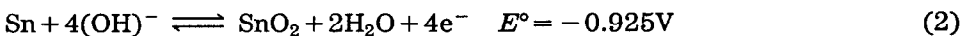


The electrode reactions are as follows

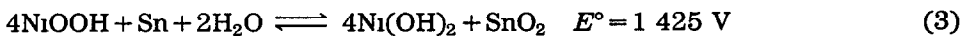
Positive electrode



Negative electrode



Overall cell reaction



The four-electron transfer supposed to take place at the tin electrode enables the system to provide high energy density, as shown in Table 1.

Studies have been reported on the silver/tin alkaline system [1]. Using a similar approach, a preliminary investigation has been made into the Ni/Sn system.

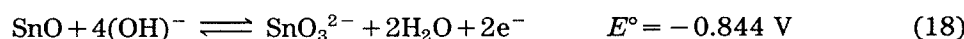
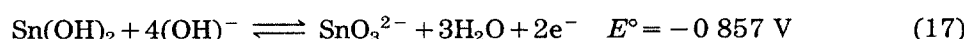
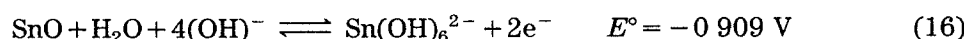
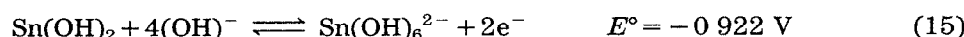
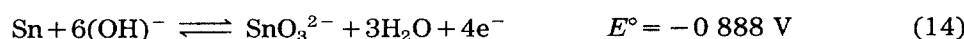
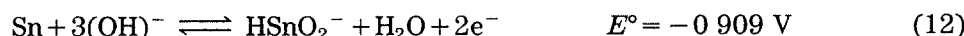
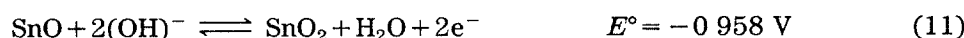
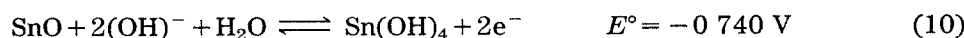
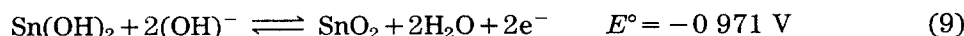
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TABLE 1

Characteristics of alkaline nickel cells

Cell	Potential (V)	Theoretical energy density (W h kg ⁻¹)
Ni/Cd	1 299	210
Ni/Fe	1 370	267
Ni/Sn	1 425	293

Tin in alkaline medium is associated with various possible electrochemical reactions [2, 3]



This list shows that there are two different reactions, (7) and (13), that involve a four-electron transfer and have an electrode potential in the region of 0.9 V

Experimental

Positive plates

A porous nickel matrix was formed by a dry powder sintering technique using a nickel-plated, mild steel substrate and carbonyl nickel powder. Nickel

powder was spread on both sides of the substrate that was kept in the cavity ($4.95 \times 5.95 \times 0.2$ cm) of a graphite plate. A number of such graphite plates were stacked into a pile and sintered for a given time in a furnace maintained at 1123–1148 K and having a hydrogen atmosphere. The plates were then cooled to room temperature. The resulting nickel matrix, with a porosity of 80–85%, was then impregnated with nickel hydroxide active material using a chemical method [4]. In this process, the porous nickel matrix was dipped into a solution of 3 M nickel nitrate and 0.25 M cobalt nitrate, dried, and then cathodised in alkali. The process was repeated until the desired loading of active material was attained. The plates were washed thoroughly to remove carbonate and nitrate ions and then dried prior to cell assembly.

Negative plates

An aqueous paste of calcium stannate active material and PTFE binder was spread onto both sides of the nickel-plated, mild steel substrate. The latter was placed on a filter paper that was then folded (to cover the plate) and subjected to a mild compaction. The pressed plate was enveloped in 3–4 layers of cellophane which served as a separator.

Cell assembly and testing

A nickel/tin cell was assembled with three nickel positives and four tin negatives. The electrolyte was 30% KOH containing 5% LiOH. The assembled cell was charged at the $C/10$ rate with an overcharge factor of 1.50. The nominal output of 1 A h was realized in the first five charge/discharge operations. The cell was subjected to cycling at different rates at a temperature of 30 ± 5 °C. A stable, uniform output of 1 A h was obtained at the $C/5$, $C/4$, and $C/3$ rates. Discharge data were plotted as

- (i) potential (E) versus time (t),
- (ii) potential (E) versus available active material (It),
- (iii) potential (E) versus current density (I)

Results and discussion

The nickel/tin cell gave an average output of 1.0 A h over 35 charge/discharge cycles. The capacity was uniform at all discharge rates, namely, $C/10$, $C/5$, $C/4$ and $C/3$. The capacity started to decrease gradually with further cycling.

Visual examination revealed that the separator had mechanically disintegrated. The variations of cell potential with time at different rates and at different cycles are presented in Figs 1 and 2, respectively. The plots of cell potential against available active material (It in A min cm^{-2}) at different current densities are shown in Fig 3. Finally, Fig 4 gives the variation of cell potential with current density.

It is seen from Fig 4 that the cell potential decreases linearly with increasing current density because of increased polarization. The plot of cell

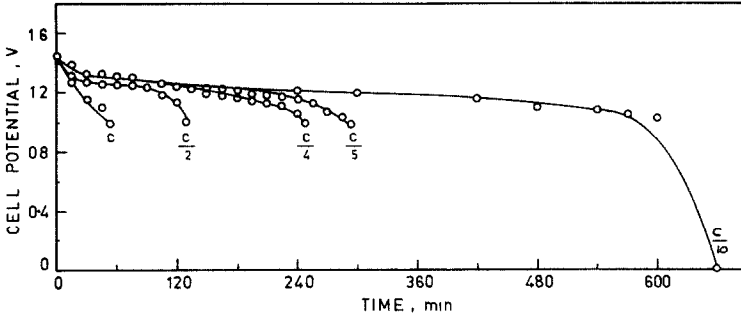


Fig 1 Discharge at various rates (rated output=1.1 A h)

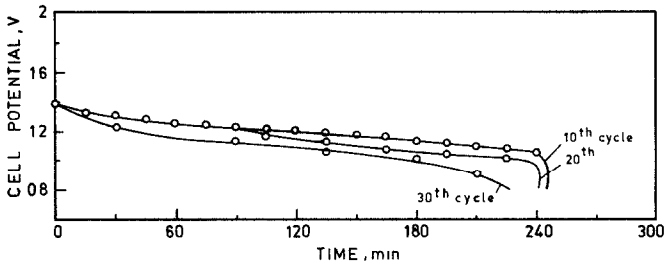


Fig 2 Discharge at 0.3 A after various cycles

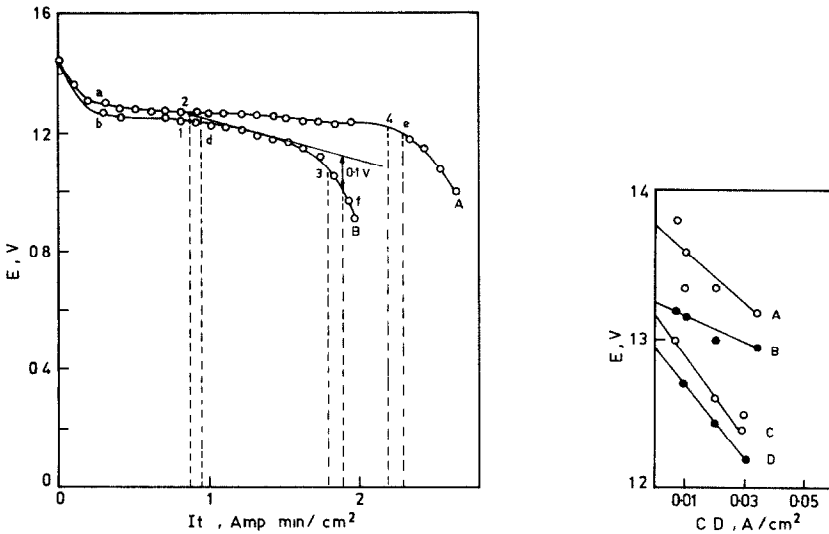


Fig 3 Potential vs available electricity A, C d = 0.0068 A cm⁻², B, C d = 0.0204 A cm⁻²

Fig 4 Potential vs current density A, It = 0.1, B, It = 0.31, C, It = 0.61, D, It = 0.81 A min cm⁻²

TABLE 2

Calculated and observed potentials of Ni/Sn cell

It (A min cm ⁻²)	Potential at $i=0.0204$ A cm ⁻² (V)	
	Calculated	Observed
0 1019	1 325	1 325
0 2037	1 323	1 316
0 3056	1 319	1 308
0 5093	1 316	1 300

potential against available active material (Fig 3) allows calculation of the internal resistance of the cell system, the polarization coefficient, and the mean available active material, as described by Shepherd [5]. Accordingly, four points, 1-4, were chosen on the linear portion of the discharge curve and another point, e, on the knee of the curve. The points, d and f, were located on the discharge curve by a suitable tangent subjected to the condition $v_b t_d = v_a t_f$. These data were then processed, using the Shepherd model, and four parameters were determined graphically as follows.

- (i) closed-circuit potential (at time $t=0$), $E_s = 1.33$ V;
- (ii) mean available active material, $Q = 1.0185388$ A min cm⁻²,
- (iii) internal resistance of the cell, $N = 4.114 \times 10^{-2}$ Ω ;
- (iv) discharge equation for the assembled Ni/Sn alkaline cell,

$$E = 1.334 - 0.7789[1.0185/(1.0185 - It)]I - (4.11463 \times 10^{-2})I$$

where E is the cell potential at any time, t , during discharge

The potential values calculated using the relationship in (iv) above, as well as the actually observed discharge potentials for a set of four values of It (at a given current density), are given in Table 2. The agreement between the observed and calculated values establishes the high reversibility of the system.

Conclusions

The present study indicates the reversible nature of the Ni/Sn system. In practice, the (gradual) sizeable decrease in capacity is attributed to the mechanical disintegration of the separator, which results in a short circuit. In order to overcome this problem, any alkali-resistant separator that is permeable only to hydrogen and hydroxide ions may be used. Additives that improve the conductivity of stannic oxide and alter the passivity of tin in alkali may lead to a practical, feasible Ni/Sn cell.

Acknowledgement

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