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Thermally activated ("thermal") battery technology Part IV. Anode materials

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ABSTRACT

In this paper, the history of anode materials developed for use in thermally activated ("thermal") batteries is presented. The chemistries (phases) and electrochemical characteristics (discharge mechanisms) of these materials are described, along with general thermodynamic properties, where available. This paper is the last of a five-part series that presents a general review of thermal-battery technology.

1. Introduction

We have reported on the history, development, and technology of thermally activated ("thermal") battery technology in earlier papers. The first paper dealt with a general overview [1], the second paper covered electrolytes [2], and the third and fourth papers dealt with cathode materials [3,4]. In this final paper of the series, we discuss anode materials.

2. Early technology

2.1. Ca and Mg anodes with WO_3 and V_2O_5 cathodes

The earlier technologies used Ca and Mg sheet (foil) anodes with WO_3 or V_2O_5 cathodes and LiCl–KCl eutectic electrolyte for fuzing application [5]. In the absence of displacement reactions with the electrolyte, these anodes would be expected to provide two equivalents per gram-atom of anode. The exact nature of the electrochemistry of these systems was not investigated in any detail but was used empirically by the thermal-battery design engineers, many of whom had little or no electrochemical background. Work was published by Laitenen et al., however, on the basic electrochemistry of V_2O_5 in molten salts [6,7]. It shows a multitude of oxidation states, leading to a series of voltage plateaus. (The high solubility of V_2O_5 – more than 17 w/o – complicated its use in thermal batteries, as it can lead to chloride oxidation in the melt.) Similar research efforts were never reported in the open literature for WO_3, however. This technology used glass tape impregnated with electrolyte for the separator.

2.2. Ca/$CaCrO_4$ couple

These earlier technologies were replaced by the Ca/$CaCrO_4$ system in the mid-1950s. From the early 1960s until into the 1970s, this couple (with an emf of over 3 V) was the primary technology for thermal batteries. (The $CaCrO_4$ replaced K_2CrO_4 that had been used earlier.)

2.2.1. Anode reactions

Since there is no separator present in the Ca/$CaCrO_4$ battery as it is constructed, the Ca anode is in direct physical contact with the $CaCrO_4$ cathode material that is dissolved in the LiCl–KCl eutectic melt (soluble to 34 w/o at 600 °C). Once the battery becomes activated, a chemical displacement reaction between Ca and the Li^+ present in the molten salt occurs, as shown in

$$2Ca + 2Li^+ \rightarrow CaLi_{2(liq)} + Ca^{2+} \quad (1)$$

Thus, a liquid Ca–Li alloy is the actual anode and not elemental Ca. This likely occurred with the earlier electrochemical systems using Ca and the LiCl–KCl eutectic. Since the anode is liquid, intercell shorting can occur if the alloy is not contained. The current collectors for the anode were undercut (smaller in diameter than the Ca) for this reason. The $CaLi_2$ discharges through several stages: $CaLi_2 \rightarrow CaLi \rightarrow Ca$. The Ca then reacts with the bulk Li^+ again (Eq.

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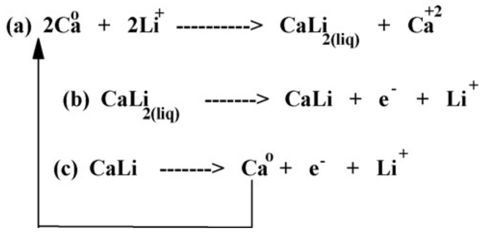

Fig. 1. Discharge reactions of Ca anode in $Ca/CaCrO_4$ thermal batteries.

(1)) to regenerate the $CaLi_2$ alloy anode. This is shown schematically in Fig. 1.

There is also the possibility of the Ca^{2+} participating in double-salt formation in the presence of K^+, as shown in

$$Ca^{2+} + K^+ + 3Cl^- \rightarrow KCaCl_{3(sol)} \quad (2)$$

The high melting point of the $KCaCl_3$ of 752 °C can cause salt precipitation at the anode–separator interface, increasing the cell impedance [8].

At the same time, the $CaLi_2$ that forms immediately reacts with the dissolved chromate to form a dark green Cr(V) compound that serves as the separator for the battery [9]. This is shown in

$$3CaLi_{2(liq)} + 4Cl^- + 17Ca^{2+} + 12CrO_4{}^{-2} \rightarrow 4Ca_5(CrO_4)_3Cl_{(s)} + 6Li^+ \quad (3)$$

Thus, both chemical as well as electrochemical reactions occur during discharge of such batteries. The chemical reactions must be controlled during discharge as they are exothermic and cause the battery to heat. Uncontrolled, they can lead to a thermal runaway where the battery destroys itself. Maintaining this delicate balance made the design of $Ca/CaCrO_4$ thermal batteries challenging.

3. Later technology

At the height of the use of the $Ca/CaCrO_4$ technology, little was known of the chemistry and materials properties that impacted performance. This resulted in much of the battery design being done empirically or based on previous experience. Later, the use of FeS_2 (pyrite) cathodes was introduced. This greatly simplified battery design because there were no major chemical reactions taking place between the electroactive components as in the $Ca/CaCrO_4$ system. In addition, the discharge mechanisms were well defined as a result of extensive work done at Argonne National Laboratory (ANL) for high-temperature, secondary applications.

3.1. Ca and Ca-alloy anodes

Some early work at ANL involved the use of Ca anodes with FeS_2 cathodes for use in high-temperature secondary batteries using LiCl–NaCl–$CaCl_2$–$BaCl_2$ electrolyte (m.p. = 383 °C) [10,11]. The work was extended to include Ca–Al, Ca–Si, Ca–Si, and mixtures of CaSi and $CaAl_2$, as well. The utilization of the Ca–Al–Si anodes was much greater than that of the Ca–Si anode. During recharge, the Ca_2Si that forms degraded the BN-felt separator that was used with Ca–Si anodes [12]. Ca anodes were also examined initially with FeS_2 cathodes at Catalyst Research Corp. (CRC) in the early 1970s but were dropped in favor of Li-alloy ones [13]. The major disadvantage of Ca anodes is the displacement reactions in the presence of Li^+ to form a liquid anode. The cell emf with Ca anodes is much less than that of Li-alloy anodes.

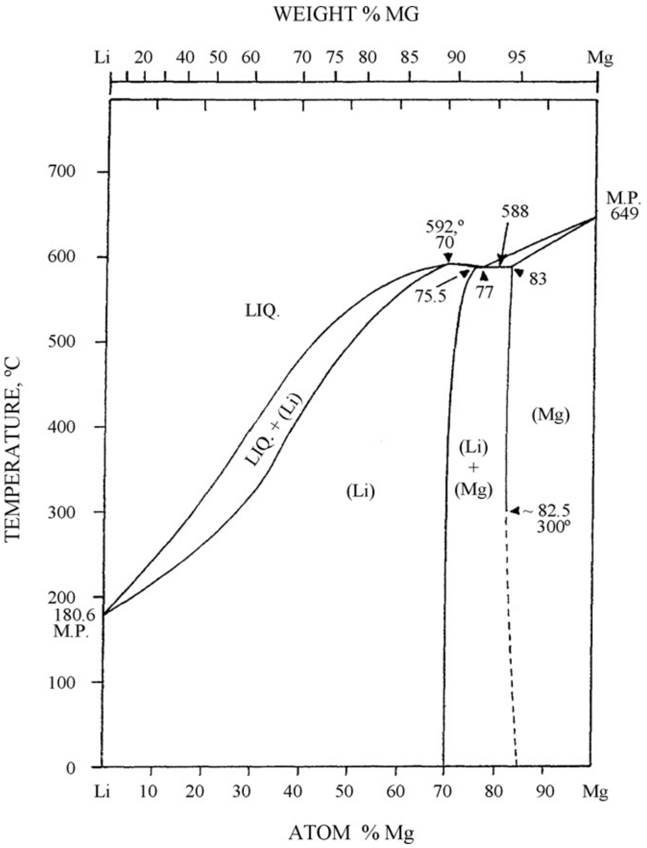

Fig. 2. Phase diagram of Li–Mg system.

3.2. Mg-based anodes

Work was done initially with the Mg/LiCl–KCl/FeS_2 system in the 1970s to demonstrate that this technology was much better than the older $Ca/CaCrO_4$ technology [14]. The use of Mg_2Si anodes containing Ca was examined at ANL for high-temperature rechargeable applications. During charging in LiCl–KCl–$CaCl_2$ electrolyte (m.p. = 350 °C), the Mg_2Si becomes a mixture of Ca–Mg–Si phases of composition $Ca_{1.5}Mg_2Si$ [15]. Problems were encountered with pure Mg, so Mg alloys such as Mg_2Al_3 and Mg_2Cu were also explored. The sluggish kinetics and lower emfs and capacities relative to the Li-alloy anodes resulted in only a limited development effort.

Mg–Si and Mg–B anodes have been reported to be rechargeable in molten-salt, high-temperature cells [16]. For this application, $MgCl_2$-containing electrolytes were used (e.g., $MgCl_2$–NaCl). However, no performance data were given.

The use of Li–Mg alloys was examined for use in high-temperature batteries. The Li–Mg phase diagram is shown in Fig. 2. The emfs of Li–Mg alloys was examined over a range of temperatures and composition in molten LiCl–KCl eutectic with the results presented in Fig. 3 [17]. No actual discharge tests were carried out with the alloys.

The diffusion coefficients in Li–Mg alloys were measured by Iwadate et al. at 420 °C by both galvanostatic and potentiostatic methods in LiCl–KCl eutectic [18]. Values for the α phase ranged from 3 to $9 \times 10^{-10}\ cm^2\ s^{-1}$. Li diffusion was much faster in the β phase, being of the order of $\sim 10^{-6}\ cm^2\ s^{-1}$.

If such alloys are to be considered for use as anodes in high-temperature batteries, the mechanical processing becomes important. With that objective in mind, Sahoo and Atkinson stud-