Calcium–bismuth electrodes for large-scale energy storage (liquid metal batteries)

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HIGHLIGHTS

- Electrochemical behavior of Ca–Bi alloys is investigated for liquid metal batteries.
- Electrochemical set-up is developed for calcium as the electro-active species (itinerant ion).
- Ca–Bi electrodes exhibit chemically reversible reactions and high coulombic efficiency.
- Electrode overpotential of Ca–Bi alloys is investigated in terms of charge transfer and mass transport.
- Co-deposition of Ba from the electrolyte improved the electrode performance.

ARTICLE INFO

ABSTRACT

Calcium is an attractive electrode material for use in grid-scale electrochemical energy storage due to its low electronegativity, earth abundance, and low cost. The feasibility of combining a liquid Ca–Bi positive electrode with a molten salt electrolyte for use in liquid metal batteries at 500–700 °C was investigated. Exhibiting excellent reversibility up to current densities of 200 mA cm^{-2}, the calcium–bismuth liquid alloy system is a promising positive electrode candidate for liquid metal batteries. The measurement of low self-discharge current suggests that the solubility of calcium metal in molten salt electrolytes can be sufficiently suppressed to yield high coulombic efficiencies >98%. The mechanisms giving rise to Ca–Bi electrode overpotentials were investigated in terms of associated charge transfer and mass transport resistances. The formation of low density $Ca_{11}Bi_{10}$ intermetallics at the electrode–electrolyte interface limited the calcium deposition rate capability of the electrodes; however, the co-deposition of barium into bismuth from barium-containing molten salts suppressed Ca–Bi intermetallic formation thereby improving the discharge capacity.

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1. Introduction

The alkaline-earth metal calcium ranks fifth among the most-abundant elements in the earth's crust, just after iron [1]. As the demand for ultra-low cost grid-scale energy storage increases, this earth-abundant and low cost metal invites scrutiny as an attractive electrode material for liquid metal battery energy storage. Liquid metal batteries comprise two liquid metal electrodes separated by a molten salt electrolyte that self-segregate into three liquid layers based upon density and immiscibility. Despite the popularity of lithium-based systems for electrochemical energy storage, recent thermodynamic and economic analyses of various liquid metal battery electrode couples indicate that calcium-based systems have higher equilibrium cell voltages and lower costs than comparable lithium systems [2]. The high reactivity and strong reducing power of calcium combined with its high solubility in molten salts disqualify the metal as an electrode. Instead, the primary use of calcium has been restricted to the extraction and refining of less reactive metals such as titanium, zirconium, and rare earth elements [1].

Historically, two types of high temperature batteries using calcium as the active component have been developed: thermally activated reserve batteries (or thermal batteries) and secondary calcium-metal sulfide batteries. In thermal battery systems, elemental solid calcium negative electrodes were used with transition metal oxide positive electrodes ($K_2Cr_2O_7$, $CaCr_2O_7$, or WO_3), and a molten salt electrolyte (LiCl–KCl). The cell reactions in a

thermal battery are complex and involve direct chemical reactions between the electrodes and the electrolyte that make it impossible to recharge the cell. These calcium-based thermal batteries were used in military applications such as missiles, ordnances, and nuclear weapons until the 1980s [3]. In the late 1970s, Argonne National Laboratory began developing calcium-metal sulfide batteries with solid calcium alloy negative electrodes (Ca–Al, Ca–Mg, or Ca–Si), metal sulfide positive electrodes (FeS$_2$, FeS, NiS, or CoS), and a molten salt electrolyte (LiCl–NaCl–CaCl$_2$–BaCl$_2$) for electric vehicle applications [4–6]. However, these efforts were discontinued as attention shifted to higher energy density lithium-based battery chemistries.

In this study, we investigate the possibility of using calcium-based liquid alloys as electrodes in liquid metal batteries for grid-scale electrochemical energy storage. The prototypical calcium-based liquid metal battery cell can be written as:

$$\text{Ca(in A)} \mid \text{electrolyte(l)} \mid \text{Ca(in B)} \tag{1}$$
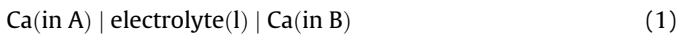
where A (e.g.; Mg, Zn, or Al) is the negative electrode host metal, and B is the positive electrode metal (e.g.; Bi, Sb, Sn, or Pb). Due to the high melting temperature of calcium (842 °C), alloying with more noble A metals is desired to lower the melting point of the negative electrode and minimize side reactions with the molten salt electrolyte. The electrolyte can be a molten mixture of alkali and/or alkaline-earth halide salts; which typically have high ionic conductivities of greater than 1 S cm^{-1}.

For this cell, the generic half–cell reactions are

$$\text{negative}: \text{Ca(in A)} = \text{Ca}^{2+} + 2e^- \\ \text{positive}: \text{Ca}^{2+} + 2e^- = \text{Ca(in B)} \tag{2}$$
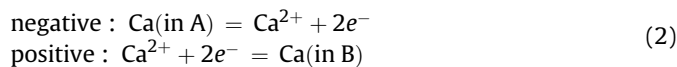
and the overall cell reaction is

$$\text{cell}: \text{Ca(in A)} = \text{Ca(in B)}. \tag{3}$$

The thermodynamic driving force for this reaction is supplied by the change in partial molar Gibbs free energy of the cell,

$$\Delta \overline{G}_{cell} = \overline{G}_{\text{Ca(in B)}} - \overline{G}_{\text{Ca(in A)}} \tag{4}$$

where the partial molar Gibbs energy $\overline{G}_i$ for each component i is given by

$$\overline{G}_{\text{Ca(in B)}} = G_{\text{Ca}}^{\circ} + RT \ln a_{\text{Ca(in B)}} \\ \overline{G}_{\text{Ca(in A)}} = G_{\text{Ca}}^{\circ} + RT \ln a_{\text{Ca(in A)}} \tag{5}$$

where a_i is the activity, G_{Ca}° the standard chemical potential of calcium, R the gas constant, and T the temperature. The change in partial molar Gibbs free energy can be related to a cell equilibrium voltage $E_{cell,eq}$ by the Nernst equation

$$\Delta \overline{G}_{cell} = -zFE_{cell,eq} \tag{6}$$

where $z = 2$ is the number of electrons exchanged in the reaction and F is the Faraday constant. From Equations (4)–(6), the cell equilibrium voltage is related to the activities of calcium in the positive and negative electrodes:

$$E_{cell,eq} = -\frac{\Delta \overline{G}_{cell}}{zF} = -\frac{RT}{zF} \ln \left(\frac{a_{\text{Ca(in B)}}}{a_{\text{Ca(in A)}}} \right). \tag{7}$$

Conceptually, the thermodynamic driving force for cell discharge can be interpreted as a stronger interaction of calcium with metal B than metal A, where low calcium activity in metal B

and high calcium activity in metal A yields a high equilibrium cell voltage. In the present study, the feasibility of a calcium-based liquid metal battery is investigated using a liquid bismuth positive electrode (B = Bi); which has a low melting temperature (271 °C) and is minimally corrosive to typical cell construction materials at elevated temperatures, such as steels.

Previous thermodynamic investigations of Ca–Bi alloys led to the development of a highly stable reference electrode; which made the evaluation of the electrochemical performance of calcium-based liquid metal alloys in this study possible [7,8]. Those emf concentration cell studies employed a CaF$_2$ solid electrolyte with low electrical conductivity, i.e., 4.4×10^{-7} to 1.8×10^{-4} S cm^{-1} at 500–700 °C [9]; a value sufficient for thermodynamic investigations, but impractical for electrochemical energy storage applications. Molten salt electrolytes typically exhibit much higher conductivities (~ 1 S cm^{-1}); however, the solubility of calcium in molten salt electrolytes and resulting electronic conductivity make accurate electrochemical measurements experimentally difficult.

The following dissolution mechanism of calcium metal into a molten salt solution was proposed [10]:

$$\text{Ca(s)} + \text{Ca}^{2+} \rightarrow 2\text{Ca}^+ \text{ or } \text{Ca}_2^{2+} \tag{8}$$

where calcium metal reacts with Ca^{2+} cations to form subvalent species Ca$_2^{2+}$ or Ca$^+$. In general, the solubility of calcium in molten salt electrolytes is reduced at lower temperatures and lower calcium activities in host metal electrodes. Previous research efforts measured pure calcium metal solubility in CaCl$_2$(l) to be 2.7–5.7 mol% at 820–1000 °C [11–13]. By contrast, Sharma [10] found that by alloying with another metal, the solubility of calcium can be significantly reduced to as low as 0.3 mol% calcium in CaCl$_2$(l) using a Ca–Cu alloy (30–70 mol%) electrode. Ukshe and Bukun [12] showed that the solubility of magnesium in MgCl$_2$(l) at 800 °C could be decreased by varying degrees by mixing the molten salt with other cation chloride salts, such as LiCl, NaCl, and BaCl$_2$, depending on the ionic size of the foreign cation species.

To suppress calcium dissolution in this study, low melting point electrolyte compositions were formulated with metal chlorides of less noble metals. Specifically, two compositions were selected: LiCl–NaCl–CaCl$_2$ (38–27–35 mol%, $T_m = 450$ °C) and LiCl–NaCl–CaCl$_2$–BaCl$_2$ (29–20–35–16 mol%, $T_m = 390$ °C) [4]. The physical and electrical properties of these are given in Table 1.

Two-phase metal alloys can serve as stable, consistent reference electrodes for highly reactive systems. For example, two-phase Li–Al alloys comprising Al(s) and LiAl(s) are commonly used as reference electrodes in lithium-bearing molten salt electrochemical cells due to the invariance of the equilibrium electrode potential with compositional changes within the two-phase regime [14]. Based upon these findings, a Ca–Bi alloy (calcium mole fraction $x_{\text{Ca}} = 0.35$) with low calcium activity ($a_{\text{Ca}} = 9 \times 10^{-10}$ at 600 °C) and solid–liquid (Ca$_{11}$Bi$_{10}$ + l) two-phase phase behavior (see Fig. 1)

Table 1
Physical and electrical properties of electrolytes.

Electrolyte	Composition/mol%	T_{liquidus}/°C	ρ^b/g cm^{-3}	σ^b/Ω^{-1} cm^{-1}	T/°C
LiCl–NaCl–CaCl$_2$	38–27–35	450^a	1.90	2.18	500
			1.85	2.58	600
			1.81	2.94	700
LiCl–NaCl–CaCl$_2$–BaCl$_2$	29–20–35–16	390	2.29	1.56	500
			2.24	1.88	600
			2.19	2.19	700

^{a} Liquidus temperature estimated from the differential scanning calorimetry (DSC) at different heating rates.
^{b} Density and electrical conductivity at given temperature was approximated from pure components.