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Electrochemical Separation of Barium into Liquid Bismuth by Controlling Deposition Potentials

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ABSTRACT

Electrochemical separation of barium from multi-component molten salt electrolyte ($BaCl_2$-LiCl-$CaCl_2$-NaCl) at 500–700 °C is demonstrated using a liquid bismuth electrode which possesses strong chemical interactions with barium. While the standard emf analysis suggests Na to be the first species to deposit in this electrolyte followed by Ca, Li, and finally Ba, barium was found to be the first species to be reduced into the bismuth electrode followed by Ca. The exceptional deposition behavior of barium was ascribed to the activity of the constituent alkali/alkaline-earth metals in the bismuth metal. The activity of barium in bismuth was extremely low (as low as 10^{-15}), shifting the redox potential of barium to the most positive potentials and enabling the separation of barium into liquid bismuth. By exploiting the differential interactions of constituent ions with the liquid bismuth, it was possible to separate conventionally non-separable barium species from the electrolyte solution. In addition, high coulombic efficiencies of the liquid bismuth electrode (>99%) suggest that electrode processes are chemically reversible for co-deposition of barium and calcium. The analyses of electrode potentials at various current densities and electrochemical impedance spectra indicate charge transfer as the most significant overpotential mechanism during electrolysis.

1. INTRODUCTION

Alkali/alkaline-earth metals are highly reactive, characterized by low standard electrode potentials, and their halides are often employed as constituents of a supporting electrolyte (as non-electroactive ions). According to the standard electrode potentials of alkali/alkaline-earth elements in the chloride system at 600 °C (Fig. 1)[1], one would expect barium metal to deposit last from a solution of alkali/alkaline-earth metal chlorides as it has the highest stability in the electrolyte, indicated by its redox potential ($E^0_{Ba^{2+}/Ba} = -3.74$ V vs. $Cl^-/Cl_2(g)$). In other words, barium is one of the most challenging species to separate from the electrolyte solution electrochemically.

While the reduction of the most stable species in the electrolyte (e.g., Ba^{2+} in the chloride system) is not feasible based upon the analysis of standard electrode potentials, we will demonstrate the feasibility of separating these stable species using liquid metal electrodes that possess preferential, strong chemical interactions with these elements. More specifically, we will present unusual deposition behavior of barium into liquid bismuth electrodes ($T_{m, Bi} = 271$ °C) from the multi-component $BaCl_2$-LiCl-$CaCl_2$-NaCl (16-29-35-20 mol%) electrolyte, based upon the thermodynamic analysis of electrode reactions at 500–700 °C. This finding is believed to occur due to the strong interaction between liquid bismuth and barium metals, switching the sequence of deposition potentials of the constituent ions.

This study also suggests that the use of strongly interacting liquid metals enables us to separate out the most stable ionic species from electrolyte solutions, providing a direct methodology to purify electrolyte solutions contaminated with stable alkali/alkaline-earth elements in electrochemical refining or separation processes. For example, in electrochemical separation of uranium from used nuclear fuels in molten salt electrolytes (e.g., LiCl-KCl), a periodic replacement of electrolyte solution is required due to the accumulation of the alkali/alkaline-earth elements (e.g., Ba^{2+}, Cs^+, or Sr^{2+}) that changes the physical and chemical properties of the electrolyte thereby generating an excessive volume of nuclear waste [2,3]. The liquid metal electrodes can separate these conventionally non-separable alkali/alkaline-earth elements from the electrolyte solution, enabling direct purification and recycling of electrolytes, as well as reduction in the volume of nuclear waste.

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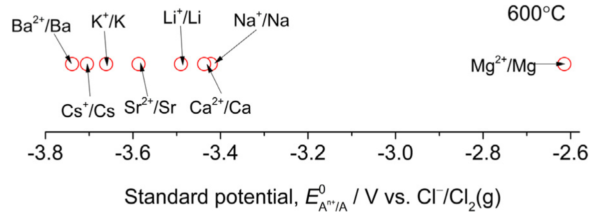

Fig. 1. Standard electrode potentials of selected alkali/alkaline-earth elements vs. $Cl^-/Cl_2(g)$, calculated based on the standard free energy of formation of pure chlorides at 600 °C [1].

Liquid metals possess unique electrochemical deposition properties due to their capacity to form an alloy phase with reduced species. These liquid metal electrodes have been widely employed in electrochemical technologies for separating target elements through selective deposition and for electrochemical energy storage devices, utilizing their inherently high electronic conductivity, high liquid-state solubility, and fast mass transport kinetics [2,4]. Because the composition of liquid electrodes changes continuously during the deposition process due to alloying reactions, the thermodynamic properties of liquid alloys such as activity should be considered in investigating the interfacial electrode processes. Obviously, the equilibrium potential of liquid alloys will deviate from the standard potentials which are defined at unit activity for both reactants and products, depending upon the thermodynamic activity values of redox species in liquid alloys.

In liquid bismuth, the thermodynamic activity values of alkali/alkaline earths (A = Li, Na, Ca, and Ba) $a_{A(\text{in Bi})}$ were determined primarily using electrochemical cells that measure the electromotive force (emf) between the pure metal (A) and the alloys (A-Bi), as summarized in Table 1 at a constant mole fraction of $x_{A(\text{in Bi})} = 0.05$ at 600 °C [5–9]. These thermodynamic properties were obtained using a LiCl-LiF electrolyte for Li-Bi, sodium-β'' alumina for Na-Bi, CaF_2 for Ca-Bi, and BaF_2 for Ba-Bi systems. The activity values of these elements in liquid Bi are extremely low and span over ten orders of magnitude ($10^{-5} < a_{A(\text{in Bi})} < 10^{-15}$), implying (i) strong chemical interactions between alkali/alkaline-earth metals with bismuth metal, (ii) a large thermodynamic driving force for alloying (reduction) reactions, and (iii) a substantial shift in the equilibrium potentials of alkali/alkaline-earths from their standard potentials. In particular, a wide range of activity values among alkali/alkaline-earth elements can lead to a unique series of equilibrium potentials, distinct from the series of standard electrode potentials.

To understand the deposition sequence of alkali/alkaline-earths into liquid bismuth, it is important to recognize that the equilibrium potential of the bismuth electrode relies on the activity values of each alkali/alkaline-earth metals which will also change as a function of composition. A generic half-cell reaction at the liquid bismuth electrode can be written as:

$$A^{n+} + ne^- = A\ (\text{in Bi}) \qquad (1)$$

, where A represents alkali/alkaline-earth elements (A = Ba, Li, Ca, and Na) and n is the number of electrons exchanged in the reaction ($n = 1$ for alkali and $n = 2$ for alkaline-earth metals). Then, the equilibrium potential of each element E_{eq} is defined as follows according to the Nernst equation:

$$E_{eq} = E^0_{A^{n+}/A} - \frac{RT}{nF}\ln\left(\frac{a_{A(\text{in Bi})}}{a_{A^{n+}}}\right) \qquad (2)$$

, where $E^0_{A^{n+}/A}$ is the standard electrode potential of the A^{n+}/A couple, R is the gas constant, T is the temperature, F is the Faraday constant, and a are the activity values of the reactant and product.

Using the above Nernst equation, the equilibrium potentials of each binary A-Bi alloy E_{eq} at 600 °C were estimated at constant mole fraction $x_{A(\text{in Bi})} = 0.05$ using the activity values of $a_{A(\text{in Bi})}$ in the pure electrolyte ($a_{A^{n+}} = 1$), as summarized in Table 1 and graphically presented in Fig. 2. Comparing the series of electrode potentials in standard states and in the liquid bismuth electrode, the deposition sequence of elements into the bismuth electrode is as follows: Ba → Ca → Na/Li, in contrast to the standard sequence of Na → Ca → Li → Ba due to a substantial difference in thermodynamic activity values among alkali/alkaline-earths in liquid bismuth. This analysis suggests that the extremely low activity value of barium in bismuth (3.7×10^{-15}) leads to the most significant potential change (1.25 V) and enables a preferential deposition of barium into a liquid bismuth electrode, in good agreement with our experimental observation where preferential deposition of barium occurs along with co-deposition of calcium.

When electrolysis is performed in $BaCl_2$-LiCl-$CaCl_2$-NaCl electrolyte using non-interacting inert electrodes (e.g., glassy carbon, tungsten, steel, or platinum), sodium metal will be reduced and deposited first onto the inert electrodes, as indicated by its highest redox potential ($E^0_{Na^+/Na} = -3.42$ vs. $Cl^-/Cl_2(g)$). In fact, sodium metal is produced by electrolytic decomposition of binary $CaCl_2$-NaCl (42-58 mol%, $T_m = 580$ °C) electrolyte at 600 °C in an industrial-scale Downs cell where sodium metal is preferentially reduced onto an inert steel cathode [10], as suggested by the analysis of standard electrode potentials (Fig. 1). In contrast, in the presence of liquid bismuth electrode in ternary LiCl-$CaCl_2$-NaCl (38-35-27 mol%, $T_m = 450$ °C) electrolyte, the preferential deposition of calcium into a liquid bismuth electrode was reported to occur over sodium at 600 °C, due to the stronger interaction (or low thermodynamic activity) of calcium-bismuth ($a_{Ca(\text{in Bi})} \sim 10^{-11}$) over sodium-bismuth ($a_{Na(\text{in Bi})} \sim 10^{-5}$) [11].

Table 1
The activity of alkali/alkaline-earths A (A = Ba, Li, Ca, or Na) in liquid bismuth $a_{A(\text{in Bi})}$ at a constant mole fraction $x_{A(\text{in Bi})} = 0.05$, standard electrode potential E^0 for each redox couple (A^{n+}/A), and the equilibrium potential of bismuth E_{eq} at 600 °C [5–9].

A^{n+}/A	$a_{A(\text{in Bi})}$	E^0/V	$-(RT/nF)\ln a_{A(\text{in Bi})}$/V	E_{eq}/V
Ba^{2+}/Ba	$3.7 \times 10^{-15*}$	−3.74	1.25	−2.49
Li^+/Li	2.5×10^{-6}	−3.49	0.48	−3.01
Ca^{2+}/Ca	3.7×10^{-11}	−3.44	0.90	−2.53
Na^+/Na	1.6×10^{-5}	−3.42	0.42	−3.01

[*] The activity of Ba in Bi was estimated by extrapolating the experimental results at 850 °C using the temperature coefficient of emf (dE_{cell}/dT) obtained from a proxy Ca-Bi system (0.18 mV K^{-1}) [8,9].

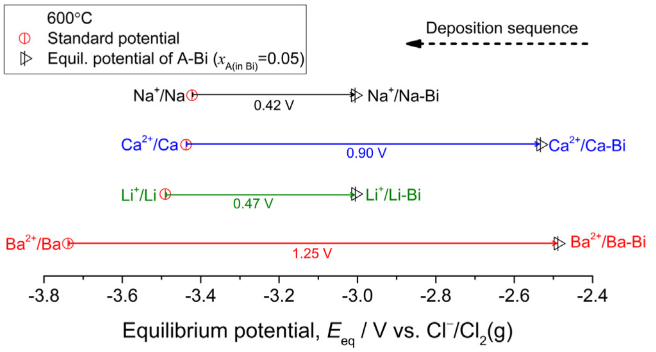

Fig. 2. Equilibrium potentials of redox couples in the bismuth electrode (open triangle) at constant mole fraction $x_{A(\text{in Bi})} = 0.05$, compared to standard electrode potential (open circle) at 600 °C. The line between the two equilibrium potentials of each species represents the shift in electrode potential due to the activity in the bismuth electrode.