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Evaluation of Alkali Bromide Salts for Potential Pyrochemical Applications

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Abstract
Transient techniques were employed to study the electrochemical behavior, reduction mechanism and transport properties of REBr₃ (RE - La, Nd and Gd) in pure LiBr, LiBr-KBr (eutectic) and LiBr-KBr-CsBr (eutectic) melts. Gd(III) showed a reversible single step soluble-insoluble exchange phenomenon in LiBr melt at 973K. Although La (III), Nd(III) and Gd(III) ions showed reversible behavior in eutectic LiBr-KBr melts, these ions showed a combination of temperature dependent reversible and pseudo-reversible behavior. While both La(III) and Gd(III) showed one step reduction, the reduction of Nd(III) was observed to be a two step process. La metal could be electrodeposited from the ternary electrolyte at a temperature of 673K. Various electrochemical measurements suggest that both binary and ternary bromide melts can potentially be used to electrodeposit high purity RE metals at comparatively lower operating temperatures.

1. Introduction
In recent times, reprocessing of irradiated nuclear fuel is being viewed as an effective tool to manage the spent nuclear fuel. The goal is to remove intensely radioactive, long-lived and high heat load radioisotopes of neptunium, plutonium, americium, curium (minor actinides), cesium, iodine, and tellurium from the used nuclear fuel, and hence reduce their inventory, in the nuclear waste, prior to disposal. The introduction of more advanced fuel cycle schemes, such as Japanese double-strata fuel cycle concept [1], coupled with the added advantages of pyroprocessing technologies (they offer the potential for more compact and hence lower cost facilities besides being able to recover the minor actinides along with plutonium and reprocess short-cooled spent nuclear fuels) has further stimulated interest in “dry” or “pyrochemical” reprocessing methods. In recent years, various pyrochemical processes have been developed to recover actinides from (i) spent metallic, nitride, and oxide nuclear fuels and (ii) high level radioactive liquid wastes [2-3].

The design of a suitable pyrochemical process does depend on the separation efficiency of actinides and lanthanides from molten salt media. The application of modern electrochemical techniques, to study actinide and rare earth chemistry in various molten fluoride and chloride based salt systems, have helped establish the early engineering evaluation of the electrochemical cell behavior [4-6]. Electrochemical refining, being a key component of the pyrochemical processes, provides a very effective method to partition the useful components of the irradiated nuclear fuels. In fact, literature abounds with the data pertaining to the electrochemical refining of irradiated metallic fuels, to recover uranium, plutonium and minor actinides, in molten chloride media ((LiCl-KCl/NaCl-KCl/NaCl-2CsCl) [6-7]. Although bromide salts are endowed with comparable thermodynamic and electrochemical properties, these salts have, however, not been attempted for
electrowinning/refining studies. Potential advantages of these salts, over chloride salts, include (i) lower operating temperature and (ii) easy recyclability of the bromine gas (bromine being a liquid at STP), generated during the electrolysis of rare earth/transition metal bromides. The present paper describes the electrochemical behavior of three representative rare-earth bromide salts (LaBr₃, NdBr₃ and GdBr₃) in three (all bromide) electrolyte systems. The paper also compares the present data with the data reported in (all) chloride systems.

2. Experimental

2.1. Materials

High purity and anhydrous (sealed in quartz ampoules under dry argon) LiBr, KBr and CsBr (-10 mesh beads, 99.999% pure, Aldrich-APL) salts and LaBr₃, NdBr₃, and GdBr₃ (99.9% pure, Alfa Aesar) were used as the electrolytes and analytes respectively.

2.2. Equipments/Instrumentation

Electrochemical measurements were carried out inside a custom-fabricated, stainless steel, argon atmosphere controlled, well type furnace, placed inside a glove box (Figure 1) [8]. The dynamic atmosphere that prevailed inside the glove box (MBRAUN) was continuously purged with laboratory-grade argon (Air Liquide) which could maintain very low levels of moisture and oxygen contents (< 0.1 ppm each). Most of the measurements were carried out under <0.1 ppm moisture and <1.2 ppm oxygen. The furnace was provided external heating by a resistance heater. Upper portion of thermal well furnace was cooled, by a glycol-based chiller, to limit the transfer heat into the glove box.

A 55mL straight-walled nickel crucible (Metal Technology), used to contain the molten bromide salts, was held by an alumina-silica support inside a larger stainless steel crucible and was electrically insulated from the thermal well by the combination of an aluminum silicate spacer and cover. The electrodes and thermocouple were held in position by an aluminum plug, placed on the furnace cover and hung through a series of thin metallic heat shields into the nickel crucible. The temperature of the bath was monitored by a calibrated, stainless steel-sheathed, chromel-alumel thermocouple (Omega Engineering), immersed directly into the molten electrolyte.

Annealed tungsten wire (1.0 mm dia., Alfa Aesar 99.99% pure), molybdenum coil, made out of 1mm. dia. (Alfa Aesar, 99.95% pure) molybdenum wire, and a 3mm. dia. and 100mm. long glassy carbon (GC) rod were used as the working, counter and reference electrode respectively. The effective area of the counter electrode was >20 times higher than that of the working electrode. All electrodes and the thermocouple sheath were rendered electrically insulating (from the metal glove box and heat shields) by sheathing them with re-crystallized alumina tubes (Omega Engineering). Electrochemical measurements were recorded using a computer-controlled Bio-Logic SAS (model, VSP) potentiostat/galvanostat using the EC-Lab software (v10.18), supplied by Bio-logic Science instruments.

![Figure 1: Experimental electrochemical cell assembly: (1) argon-atmosphere glove box (2) cooling jacket (3) resistance heater (4) nickel crucible (5) alumina-silica centering plates inside stainless steel crucible (6)](image-url)
3. Results and Discussion

3.1. LiBr-GdBr₃ System

To our knowledge, pure LiX (where X=F, Cl, Br) melt has not been reported, in the literature, as an electrolyte for the rare earth halides. So, before proceeding to investigate the electrochemical behavior of REX₃, X=La, Nd, Gd) in binary and ternary bromide melts, we chose to first investigate the electrochemical behavior of one of the rare earth bromides (GdBr₃) in fused LiBr electrolyte.

Like the CV of GdCl₃ in eutectic LiCl-KCl melt [9], the CV of GdBr₃ in LiBr melt (Fig. 2) indicated one step reduction of gadolinium ion (Gd³⁺) to gadolinium metal (Gd⁰). Also, the value of cathodic current peak did not change significantly at different scan rates (0.025 to 0.15Vs⁻¹) (Fig. 3), which indicated the reversibility of the soluble-insoluble exchange phenomena. Such a behavior is commonly observed for most of the rare earth chlorides in the LiCl-KCl melt. The electrochemical reduction of Gd(III) in LiBr melt was diffusion-controlled and the diffusion coefficient (determined by the use of Sand’s equation) was estimated to be 1.28×10⁻⁵ cm²s⁻¹ at 923K. Although Gd³⁺ showed identical behavior in both the LiCl-KCl-GdCl₃ and LiBr-GdBr₃ melts, the latter, however, did not offer any advantage in terms of lower operating temperature. That is why, further electrochemical investigations were carried out only in eutectic LiBr-KBr and LiBr-KBr-CsBr melts.

3.2. Eutectic LiBr-KBr Electrolyte System

Experimentally determined melting point of eutectic LiBr-KBr (mol%, 60LiBr-40KBr) was determined to be in the range 600.8 – 601.7°C [10] (literature value is 601K). The melting point of eutectic composition of LiCl-KCl (mol%, 59.5LiCl-40.5KCl) is 352°C. So from a temperature standpoint, the LiBr-KBr melt does not offer any significant advantage over the LiCl-KCl melt. Figs. 4(A, B) show the cyclic voltammogram of Gd³⁺ in eutectic mixtures of LiBr-KBr (4A) and LiCl-KCl (4B) melts. A small cathodic peak, during the reverse scan in anodic region, after bromine evolution, perhaps suggests the reduction of bromine to bromide ion (0.5Br₂ + e⁻ = Br⁻).

Figure 2: Cyclic voltammogram showing Gd deposition and stripping reactions; GdBr₃ content-0.5 wt.%; WE- W wire, CE-Mo coil, RE-GC, WE area-0.16 cm², melt temperature-973K, Scan rate-0.05Vs⁻¹, Gd deposition on W took place at ~ -1.3V with reduction and oxidation peak currents being -1.37V and -1.31V respectively.

Figure 3: Cyclic voltammograms obtained for Gd³⁺ at different scan rates, in LiBr-GdBr₃ melt; [Gd³⁺]= 0.5 wt.%; W working electrode (S=0.16cm²), Mo coil - CE, GC - RE, melt temperature-973K

Gadolinium deposition and stripping, in bromide melt, took place at less negative
potentials than that observed in the chloride melt \( (I_{pc}: -1.46\,\text{V} \text{ and } I_{pa}: -1.27\,\text{V}) \) respectively. The cathodic current peak height \( (I_{pc}) \) was observed to be comparatively much smaller \((9\,\text{mA} \text{ at } 50\,\text{mVs}^{-1}) \), however at higher scan rates this current was found to increase, for example \(23\,\text{mA} \text{ at } 200\,\text{mVs}^{-1}) \) as compared to that of the anodic current peak \( (I_{pa}) \). Such type of behavior has also been reported, by several authors, in chloride media. There was a tiny current response in the anodic region \((7\,\text{mA}, \text{ between } 0-0.5\,\text{V}) \) before bromine evolution, which perhaps indicated the removal of adsorbed gaseous species from the Mo surface. Moreover, in the absence of a corresponding cathodic peak, it can be presumed that Mo didn’t actually undergo any oxidation prior to bromine evolution. A small cathodic peak, during the reverse scan in anodic region, after bromine evolution, perhaps suggests the reduction of bromine to bromide ion \((0.5\text{Br}_2 + e^- = \text{Br}^-) \). Such type of behavior has also been reported to take place on a molybdenum electrode, where chlorine evolution took place in the LiCl-KCl eutectic melt [11]. As a comparison, a cyclic voltammogram of LiCl-KCl-GdCl₃ (Fig. 4B) [9] showed the appearance of the Gd couple at comparatively more negative potential \( (I_{pc}: -2.23\,\text{V} \text{ and } I_{pa}: -2.04\,\text{V}) \) respectively than that obtained in the case of GdBr₃ (present study). This was expected as the free energy change (and hence the standard electrode potential) of the decomposition of GdBr₃ (leading to the evolution of bromine gas) is less than that of the GdCl₃. The electrochemical reduction of Gd(III), in LiBr-KBr-GdBr₃ melt, can be considered as a diffusion controlled process and the diffusion coefficients, calculated using the Sand’s equation, was determined to be \(0.21 \times 10^{-5}\,\text{cm}^2\,\text{s}^{-1}\). The reported value in the LiCl-KCl-GdCl₃ melt is \(0.31 \times 10^{-5}\,\text{cm}^2\,\text{s}^{-1}\) [9]. The formation of reddish brown color on the alumina sheath of the Mo electrode confirmed the formation of bromine gas, as the decomposition product of GdBr₃, during both the CV and CP test runs.

Like GdBr₃, the CV of LaBr₃ showed one pair cathodic and anodic peaks (Fig. 5A). NdBr₃, on the other hand, showed two pair of redox peaks (Fig. 5B) which suggests that perhaps the reduction of Nd took place in two step process \( (\text{Nd}^{3+} \rightarrow \text{Nd}^{2+} \rightarrow \text{Nd}^0) \). The corresponding chlorides \( (\text{LaCl}_3 \text{ and NdCl}_3) \) have been reported to show similar behavior.

![Figure 4: Cyclic voltammogram showing the potential window in (A) eutectic LiBr-KBr-GdBr₃ and (B) LiCl-KCl-GdCl₃ at 723K; cathodic (forward) scan shows just two current responses (Gd and Li deposition), corresponding anodic (reverse) scan shows the respective stripping peaks, also anodic scan shows the evolution of bromine and chlorine gas respectively at the CE ; (A): WE- W wire, CE-Mo coil, RE-GC, WE area-0.3cm², Scan rate-50mVs⁻¹, [Gd³⁺]-0.5wt.%; (B): WE-W, CE-vitreous carbon, RE-Ag/AgCl (0.75mol kg⁻¹ in LiCl-KCl), [Gd³⁺]-2.03x10⁻²mol/kg, Scan rate – 200mVs⁻¹, WE area – 0.352 cm², X and Y axes represent current and potential respectively](image)
in the LiCl-KCl electrolyte [12-13]. Unlike in the chloride melt, the CVs of LaBr$_3$ and NdBr$_3$, in LiBr-KBr, could be obtained at a temperature as low as 598K.

![Graph showing deposition of La and Nd on W electrode](image)

**Figure 5:** CV showing the deposition of (A) La and (B) Nd on the W electrode, operation parameters; (A) - melt temperature-773K, scan rate-0.2Vs$^{-1}$, S-0.22cm$^2$, [La$^{3+}$]-1.0 wt.%; (B) – melt temperature-698K, Scan rate-0.075Vs$^{-1}$, [Nd$^{3+}$]-1.0 wt.%, S-0.28cm$^2$

### 3.3. Eutectic LiBr-KBr-CsBr Melt

This ternary system, being one of the lowest-melting in the alkali/alkaline earth metal halide systems, offers clear definite advantage over its chloride counterpart. The reported and measured melting points of the eutectic compositions (mol%, 56.1LiBr-18.9KBr-25CsBr) are 498K [14] and 512K respectively [10]. The reported melting point of the ternary chloride composition is 536K. Although CVs could be recorded in the temperature regime 523-673K, the slopes of both cathodic and anodic current peaks were relatively smaller in the temperature range 523-573K. This may be due to the existence of the relatively larger ohmic drop (a combination of ohmic drop, activation and concentration overpotentials). Such an observation has also been made by others [15]. This is one of the drawbacks of carrying out electrochemical measurements at much lower temperatures. That is why, electrochemical reduction and refining are often carried out at slightly higher temperatures (than the eutectic melting point) to take care of these overpotentials.

The LiBr-KBr-CsBr-GdBr$_3$ system presented some interesting observations. Although Gd deposition and dissolution could be observed at a temperature as low as 573K, the kinetics of the process was observed to be inherently slow. Moreover, appearance of multiple peaks in the cathodic region and shifting of the potentials towards more negative values (even at comparatively lower sweep rates) clearly hinted at the process irreversibility. However, with a rise in temperature, both cathodic and anodic peaks were observed to be sharp which indicated a relatively faster kinetics. At 773K, the Gd(III)/Gd couple showed a single pair of reversible peaks. Reduction of Nd(III) showed identical patterns. Unlike, both Gd(III) and Nd(III), the reduction of La(III) in the ternary melt was observed to be a single step process both by CV and SQV measurements (Figs. 6 A and B) at lower temperatures. At temperatures >673K, the CV of La(III) showed two peaks which perhaps indicated that the reduction took place in two steps (La$^{3+}$→La$^{2+}$→La$^{0}$).

The CVs of REBr$_3$ (RE-La, Nd, Gd), in both binary and ternary bromide electrolytes, indicate that like in the case of chloride melts, use of reactive working electrodes, such as aluminum [12] and copper, will
alloy these metals with the WE and as a result it will, in principle, be possible to preferentially remove lanthanides and/or actinides from bromide based melts at comparatively lower temperatures.

![Figure 6](image)

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**4. Electrowinning and Electrorefining REBr3 in Binary and Ternary Bromide Melts**

Determination of the melting point of the eutectic LiBr-KBr compositions, containing up to 10 wt.% GdBr3, showed just one melting point which is the eutectic melting point (601K). Higher compositions of GdBr3 (>10 wt.%) shifted the melting temperature to higher values [10]. This suggests that the electrorefining of rare earth bromides can, in principle, be carried out in such a melt at temperatures <673K. In case of the ternary electrolyte, electrorefining can be carried out in the temperature range 523-623K. However, in order to obtain better quality metal deposit and higher throughput, an optimum temperature has to be established for the individual RE metals, which, perhaps will be higher than 673K and 623K respectively. In order to study the feasibility of the electrodeposition of La from the LiBr-KBr-1wt.%LaBr3 melt, a constant potential electrolysis at -2.1V (vs. GC) was carried out for 5 min., at 673K. The ICP-AES analysis of the salt-coated deposit (Fig. 7) suggests that the major component of the deposit was lanthanum. In the case of the electrowinning of RE bromides because of the requirement of relatively higher amounts of the solutes, the melting point of the resultant electrolyte will shift to higher values than the eutectic temperature. On the other hand, as the electrorefining requires relatively less amounts of the functional electrolyte (~10 wt.%), both the binary and ternary electrolytes are expected to provide a relatively lower temperature path for electrodepositing high purity RE metals.

![Figure 7](image)
chloride counterparts, have comparable thermodynamic and electrochemical characteristics. These studies further indicate that the applied electrochemistry of \( \text{REBr}_3 \) in alkali bromide melts might offer a comparatively low-temperature path to electrodeposit high purity RE metals. Also a reactive electrode, such as Al, can potentially be used to prepare Al-RE based intermetallic compounds/alloys from the ternary electrolyte in the temperature range 523-623K.

References