



On the use of liquid metals as cathode in molten fluorides



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ABSTRACT

The aim of this article is to investigate the behaviour of liquid metallic electrodes in pyroprocesses. Thus, studies of electrochemical properties of various liquid metallic electrodes (Bi, Sb, Sn, Pb, Ga) were performed in LiF–NaF (750 °C) and LiF–CaF₂ (850 °C). Thanks to linear sweep voltammetry technics, electroactivity domains were determined as well as a reactivity (Sb > Bi > Pb > Sn > Ga > Mo) and a nobility scale (Ga < Sn < Pb < Sb < Bi < Mo), valid in both solvent: from these data, the extraction yield of an element can be evaluated. Then the preparation of alloyed cathodes for reductive extraction process, corresponding to a spontaneous reaction between a reducing agent contained in the liquid metal and the element to be removed from the molten salt, was examined. The in situ generation of liquid Bi–Li, Na or Ca (reducing agents) reactive electrodes was performed in LiF–NaF and LiF–CaF₂ solvent by galvanostatic electrolyses. Elementary analyses showed that Li⁺ and Ca²⁺ were reduced on Bi at the same reaction rate in LiF–CaF₂, whereas Na was preferentially inserted into Bi, compared to Li, in LiF–NaF. Linear relationships between the electrolysis potential and the logarithm of the global mole fraction of reducing agent were found. As a consequence, by fixing the potential at the end of the electrolysis, Bi reactive cathodes with a controlled quantity of reducing agent can be produced in galvanostatic conditions.

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1. Introduction

Pyro-electrometallurgy is commercially used to recover or refine metals, including large scale fabrication for metals, such as liquid aluminium production. The value of using liquid cathode is evidenced by many advantages: a complete physical separation between the electrolyte and the produced metal, a constant surface area of the electrode, and an easier coalescence of microdrops and metallic fog.

Therefore, liquid metals research has been transferred to nuclear applications for pyrochemical reprocessing of irradiated nuclear fuels. In the frame of Partitioning and Transmutation concept (P&T) [1], goals are to reduce the radiotoxicity and the volume of nuclear wastes in the back-end of fuel cycle. Several processes have thus been developed to selectively recover minor actinides from nuclear fuel on a liquid metal cathode. In pyrochemical treatment, the main steps are either the electrorefining or the reductive extraction, based both on a contact between a molten salt and a liquid metallic system. The use of liquid metal electrodes allows a group recovery of metals, captured as an alloyed compound: a safe recovery is then ensured (proliferation resistant) and metals are thermodynamically stabilised. Moreover, diffusion coefficients in the salt and into the liquid metal have the same order of

magnitude, e.g. for uranium [2,3] in LiCl–KCl and in Cd at 450 °C: compared to intermetallic diffusion in a solid electrode, diffusion in the liquid is faster.

In the electrorefining process, the metallic fuel is anodically dissolved into a molten salt and most of uranium is selectively recovered on a solid cathode whereas the transuranic elements and uranium are collected on a liquid metallic pool, leaving the fission products in the salt. In Japan, investigations were performed in LiCl–KCl on liquid Cd cathode [4–7] on a wide range of alkaline earths (Sr, Ba...), rare earths (Ce, Nd...) and minor actinides (Np, Am...). Authors determined the activity coefficients, the separation factors, the mass transfer coefficients between the molten salt and the liquid phase. Parallel developments were realised for instance in the US [8–10] and in Korea [11,12] on the same systems.

Concerning the liquid–liquid extraction metallic ions are recovered into a metallic pool directly by electrolysis or using metal reducing agents (RA), as alkaline or alkaline earth elements. In the reductive extraction a spontaneous reaction between RA (oxidation) contained in a liquid metallic pool and the element to be extracted in the salt (reduction) takes place. A transfer of the element is observed from the salt to the liquid electrode in the metallic form. Numerous studies were dedicated to this technique in chloride salts, where Bi [13] and Cd [14] were mainly investigated as metallic pools and compared [15] in LiCl–KCl. Tests on a Zn liquid electrode were also made with Li [16] or Mg [17] as RA.

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However, few studies have been conducted in fluoride salts. In LiF–BeF₂, Bi–Li alloy in contact with rare earths and actinides was used to evaluate the kinetic parameters [18] and distribution coefficients [18,19]; in the same solvent, Bi, Sn, Cd and Zn were examined as metal phases [20]. More recently, LiF–AlF₃ eutectic mixture with Al as RA was identified to be very promising [21,22].

All the authors agree that the separation performances are highly influenced by the choice of the metallic cathode. Fundamental investigations are thus needed to select good candidates to be used in both electrorefining and reductive extraction processes.

Liquid metallic cathodes such as gallium (Ga), lead (Pb), tin (Sn), antimony (Sb) and bismuth (Bi) in molten LiF–CaF₂ at 850 °C and LiF–NaF at 750 °C were examined. As preamble, the main physico-chemical properties of metals are presented and discussed. The first part is dedicated to the electrochemical behaviour of the liquid metals, investigated by linear sweep voltammetry, to sort their reactivity and nobility. Then, the in situ generation of electrodes, composed of Bi liquid metal and RA (Li, Na, Ca), was considered for reductive extraction process in LiF–CaF₂ at 850 °C and LiF–NaF at 750 °C. Galvanostatic electrolyses were performed on Bi and cathodes were analysed by ICP-AES. From these data, general relationships between the amount of species and the electrolysis potential were found.

2. Experimental

2.1. The cell

The cell was a vitreous carbon crucible placed in a cylindrical vessel made of refractory steel and closed by a stainless steel lid cooled by circulating water. The inside part of the walls was protected against fluoride vapours by a graphite liner. The experiments were performed under an inert argon atmosphere (less than one ppm O₂), previously dehydrated and deoxygenated using a purification cartridge (Air Liquide). The cell was heated using a programmable furnace and the temperatures were measured using a chromel–alumel thermocouple.

The electrolytic bath consisted of an eutectic LiF–CaF₂ (Carlo Erba Reagents 99.99%) mixture (79.5/20.5 M ratio) and LiF–NaF (Carlo Erba Reagents 99.99%) mixture (60/40 M ratio), initially dehydrated by heating under vacuum (10^{−5} bar) to its melting point for 72 h.

2.2. Electrodes

Molybdenum wire (Goodfellow 99.99%, 1 mm diameter) was used as a solid working electrode. Metallic pellets of Bi, Sb, Pb, and Sn and liquid metallic Ga (Goodfellow 99.99%) were used for

the liquid working electrodes. The auxiliary electrode was a vitreous carbon (Mersen spectroscopic quality) rod (3 mm diameter) with a large surface area (2.5 cm²). The surface area of the solid working electrode was determined after each experiment by measuring the immersion depth in the bath.

The potentials were referred to a tantalum reference electrode: K₂TaF₇ (2 mol%) and a Ta wire (Goodfellow 99.99%) enclosed in boron nitride (BN, AX05 grade), in contact with the solution through a 0.2 mm hole.

Liquid electrodes (around 1.6 g of metal) were contained in boron nitride (BN, AX05 grade) and a scheme of the assembly is presented in Fig. 1. The current feeder was a molybdenum wire (1 mm diameter) immersed in the liquid metal and the contact between the salt and the metal was done by a hole in the BN wall (surface area of contact: 0.41 cm²).

2.3. Techniques

The electrochemical study and the electrolyses were performed with an Autolab PGSTAT30 potentiostat/galvanostat controlled with the GPES 4.9 software; cyclic voltammetry, linear sweep voltammetry and galvanostatic electrolyses were used.

Bi, Li, Na and Ca contents in the liquid cathode were measured, after dissolution in an equimolar mixture of pure nitric and hydrochloric acids, using Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP–AES, HORIBA Ultima 2).

3. Results and discussion

3.1. Liquid metal selection

The handling of liquid metal is constraining as the liquid electrode container has to be chemically inert to both fluoride salts and liquid metals, and also insulating as the cathode is polarized. Only few materials fulfil these criteria and among of them, boron nitride was chosen. In order to select metals for liquid electrodes, some conditions should be respected:

- The metal has to be liquid at the operating temperature for both fluoride solvent: 850 °C in LiF–CaF₂ and 750 °C in LiF–NaF. Moreover, the metal should not boil for a better use of the liquid cathode. These limitations define a range of temperature where the working temperature should be between the melting point and the boiling point of the metallic element.
- A large difference in density at the operating temperature is required between the metal and the electrolyte. In our experiment, the liquid metal has to be denser than the molten fluorides, which are 2.04 g cm^{−3} for LiF–CaF₂ at 850 °C and 1.96 g cm^{−3} for LiF–NaF at 750 °C [23].
- As the liquid metal is in equilibrium with its saturated vapour pressure, a low vapour pressure at operating temperature is requisite to avoid metal distillation.

Melting and boiling points, density and vapour pressure of bismuth (Bi), gallium (Ga), lead (Pb), antimony (Sb) and tin (Sn) are gathered Table 1: these elements strictly respect each conditions and were used as liquid metallic electrode.

3.2. Electrochemical properties of liquid metals

In this part, the behaviour of liquid electrodes was studied by electrochemical measurements (oxidation and reduction). Linear sweep voltammetry was performed at 10 mV s^{−1} in LiF–CaF₂ at 850 °C and in LiF–NaF at 750 °C on Ga, Pb, Sn, Sb, Bi, and Mo. An

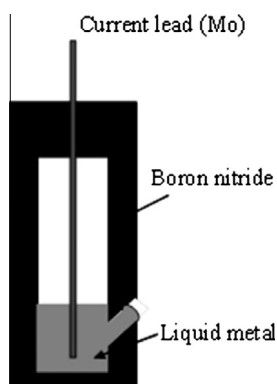


Fig. 1. Scheme of a typical liquid metal electrode.

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