



Full communication

Electrochemical extraction of lanthanum in molten fluoride salts assisted by KF or NaF

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ABSTRACT

Separation of some active metal ions such as Ce^{3+} , Eu^{3+} , and La^{3+} from molten fluoride salt using electrochemical process is difficult. The currently available electrodeposition process assisted by the solid reactive electrode or liquid metal electrode faces challenges such as the isolation of the reactive electrode due to the formation of a compound, the ability to maintain a low activity value of the active metal in liquid electrode, and a complex purification process of the target metal. In the present study, we developed a new method that successfully proved the extraction of lanthanum from molten LiF salt using an inert Mo electrode with the assistance of either NaF or KF salt. In that case, the formation of LaF_6^{3-} in LiF-KF (or LiF-NaF) salt, instead of La^{3+} in LiF, positively shifts the electrodeposition potential of lanthanum by a value of about 1 V. The simplicity of this method compared to the conventional routes for the extraction of lanthanum from molten salt will result in a reduction in separation costs and this approach has a potential application for the separation of other active metals in molten fluorides or chlorides.

1. Introduction

Electrochemical deposition of metals plays an important role in many modern technologies. For instance, it provides a unique opportunity to produce metals [1] and has successfully realized the preparation of pure titanium without complicated and expensive procedures [2]. Electrochemical deposition of rare earth metals on Pd substrate is treated as a new and good method for the fabrication of high temperature hydrogen adsorbing and permeable alloys: Pd-rare earth alloys [3]. To produce high purity rare earth metal which has great use in many modern technologies, including the generation of catalytic filter-neutralizers of exhaust gases of cars, fiber optics, lasers, oxygen sensors, and superconductors [4], electrochemical deposition in molten salts is regarded as a promising method [5]. In the nuclear industry, electrochemical deposition is proposed to recover fissionable uranium and plutonium from spent nuclear fuel [6,7] and separate fission products for molten salt reactor coolant clean-up process [8–10].

Electrochemical deposition can be typically done in a three-electrode cell system (working, counter, and reference electrodes). Through applying with a proper electrical potential or a current, the target metal ions in the electrolyte will be concentrated and deposited on the working electrode. This step is carried out at a potential which is more negative than the equilibrium potential of the target metal ion. For metal ions whose potential for deposition is more positive than the

cathodic limit of the electrolyte, a simple inert working electrode can be applied to easily deposit the target metals. However, it will become invalid in the case of the electrodeposition of active metal ions whose equilibrium potentials are close to (or more negative than) the cathodic limit of the electrolyte. The most frequently used method for this situation is performing with a liquid or solid reactive metal working electrode [11,12,14].

When using a liquid metal electrode, the equilibrium potential of the metal to be deposited can be written as

$$E_{eq(\text{in liquid metal})} = E_{A^{n+}/A} - \frac{RT}{nF} \ln(\alpha_A \text{ (in liquid metal)}) \quad (1)$$

where $E_{A^{n+}/A}$ is the equilibrium potential when pure A is deposited on an inert material, R is the gas constant, T is the working temperature, F is the Faraday constant, n is the electron transfer number and α is the activity of A in the liquid metal. Comparing with common inert electrodes, a liquid metal electrode makes the electrodeposition of the target metal ions proceed at a more positive potential, especially when the activity of the target element in liquid metal is extremely small. For example, with a liquid bismuth electrode in which the activity of barium metal is only 3.7×10^{-15} , barium ions have been successfully separated from $BaCl_2$ -LiCl-CaCl₂-NaCl molten salt at 773–973 K [11].

If a reactive solid metal working electrode is used, the half-reaction of the electrodeposition of target metal ions, A^{n+} , on a reactive

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Table 1

Calculated standard reduction potentials of LaF₃/La, LiF/Li, NaF/Na, KF/K, and K₃LaF₆/La.

Redox couple	Standard reduction potential E° (V vs. F ₂ /F ⁻)
LiF/Li	-5.38
NaF/Na	-4.85
KF/K	-4.83
LaF ₃ /La	-4.99
K ₃ LaF ₆ /La	-3.97

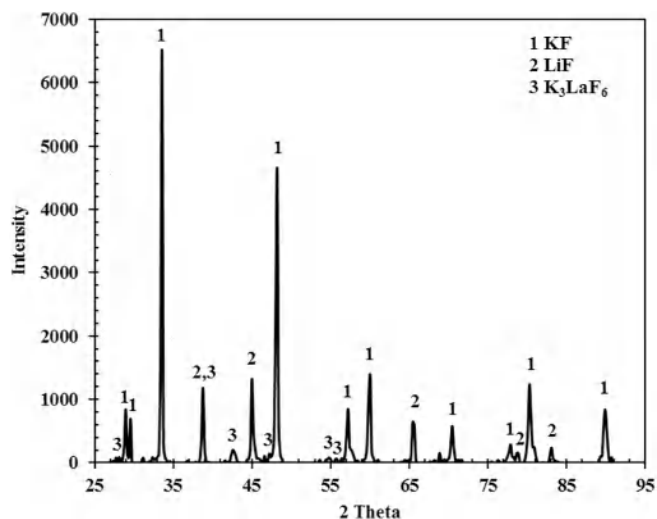


Fig. 1. XRD analysis result of the quenched eutectic LiF-KF-2.73 wt% LaF₃ molten salt.

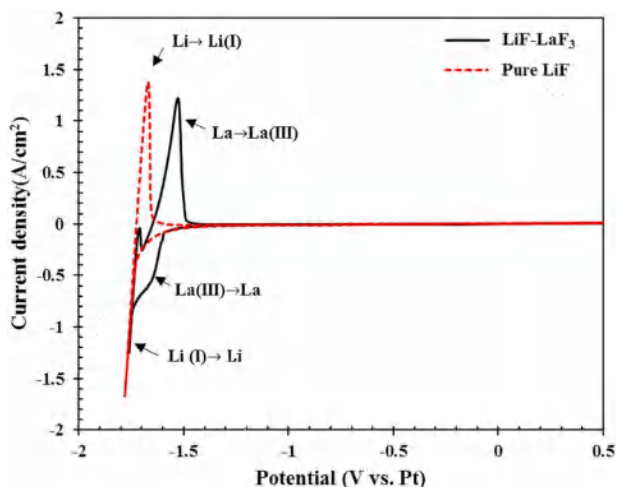


Fig. 2. Cyclic voltammograms obtained in LiF-LaF₃ and pure LiF molten salts. Scan rate: 100 mV/s; working electrode: Mo; counter electrode: graphite; LaF₃ = 3.33 wt%; $T = 1173$ K.

electrode, B , is written as



Then the equilibrium potential of A^{n+}/A_xB_y is

$$E_{A^{n+}/A_xB_y} = E_{A^{n+}/A} - \frac{1}{x} \frac{\Delta G(A_xB_y)}{nF} \quad (3)$$

where $\Delta G(A_xB_y)$ is the Gibbs free energy of formation of compound A_xB_y . The value of E_{A^{n+}/A_xB_y} will be more positive than $E_{A^{n+}/A}$ if the value of $\Delta G(A_xB_y)$ is negative and the electrodeposition of A^{n+} will happen at a potential more positive. Electrodepositions of Eu in LiCl-

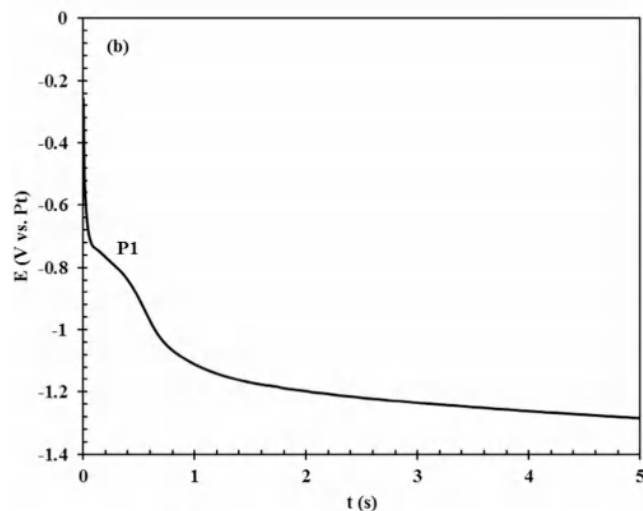
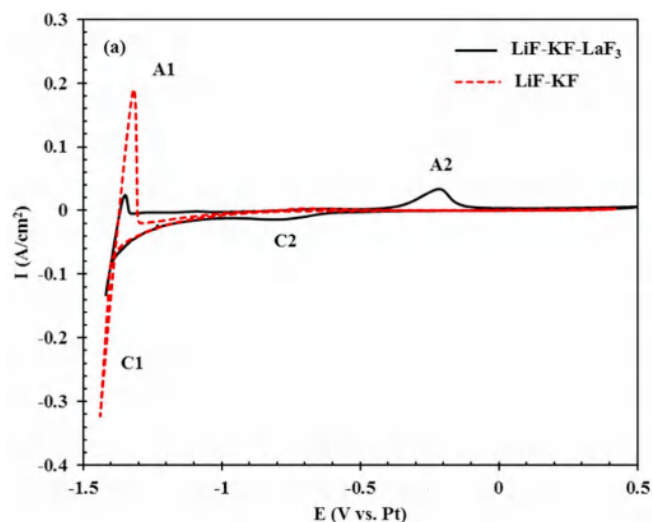


Fig. 3. (a) Cyclic voltammograms obtained in LiF-KF eutectic molten salt with LaF₃ dissolved in and pure LiF-KF eutectic molten salt at the scan rate of 200 mV/s. (b) Chronopotentiogram of the system of LiF-KF-LaF₃ with the applied current of -50 mA (working electrode area = 2.24 cm²). Working electrode: Mo; counter electrode: graphite; LaF₃ = 2.73 wt%; $T = 973$ K.

KCl molten salt [13] and lanthanides in LiF-CaF₂ molten salt [14] have been realized successfully through this method.

Although the application of liquid metal electrode and solid reactive electrode could proceed the electrodeposition of target metal ion at a more positive potential, there are a series of issues accompanying it. For instance, to get a successful deposition of active metal into the liquid metal electrode, the activity of the active metal in the liquid electrode needs to be kept at a low value. Considering the activity will increase with concentration, the liquid electrode is not capable of depositing the active metal on a large scale. When using a solid reactive electrode, the formed compound on its surface could isolate the reactive electrode and the further deposition of active metal becomes impossible. Furthermore, to get the pure target metal, an additional purification process is needed to separate it from the formed compound or liquid metal electrode, which will increase the separation costs.

The electrochemical deposition of lanthanum in molten salt is essential for the coolant clean-up in molten salt reactor [15,16]. In the present study, instead of employing the two methods discussed above, the electrodeposition of lanthanum from molten fluorides will be achieved in a simpler way. LiF is a main constituent of most proposed molten salt coolant candidates in nuclear energy applications [17]. The

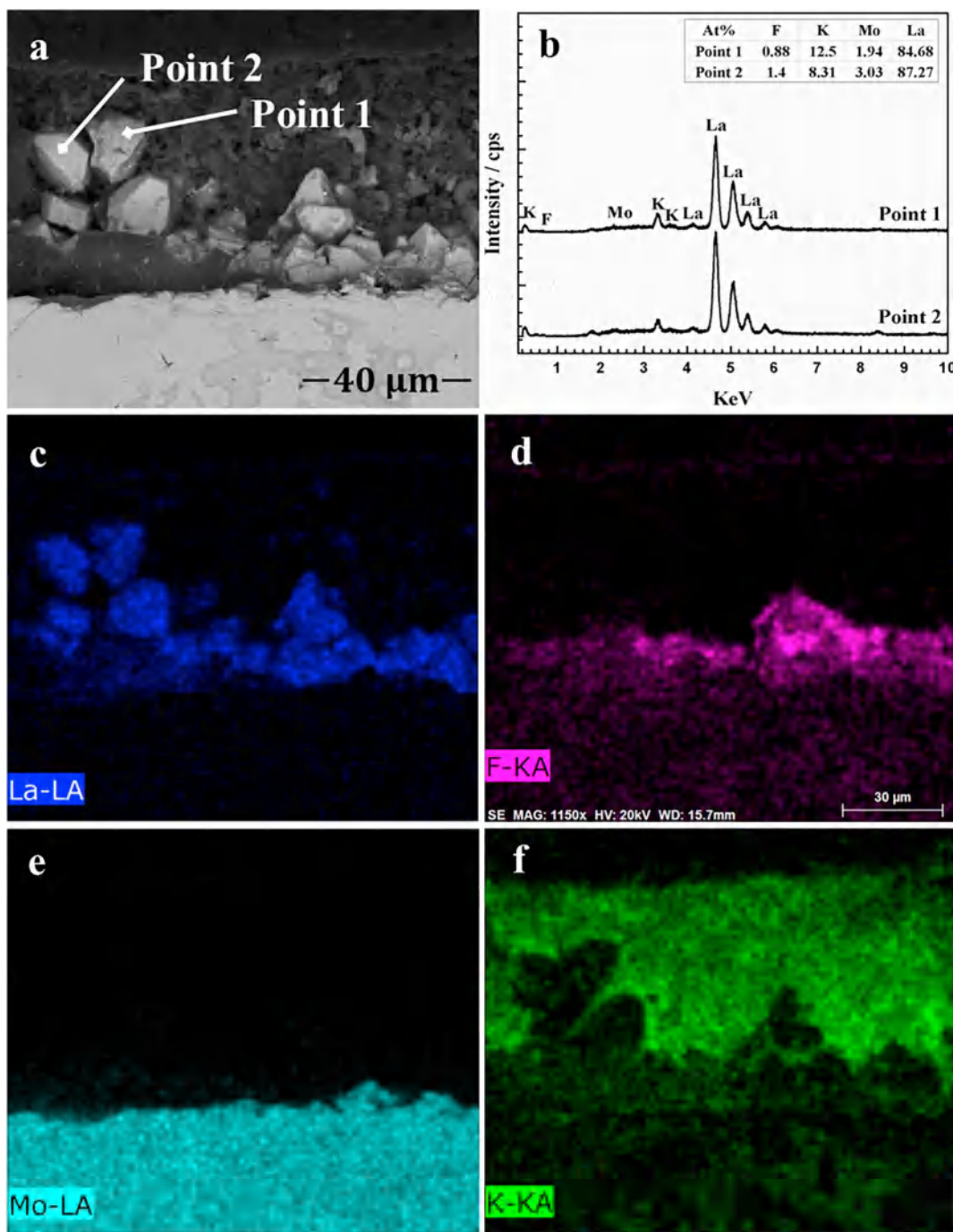


Fig. 4. (a) Backscattered electrons (BSE) image of the cross-section of polished Mo rod electrode after electrolysis in LiF-KF-LaF₃ molten salt; (b) EDS point scan results of point 1 and point 2 in Fig. 4a; (c)-(f) EDS mapping results of Fig. 4a.

standard reduction potentials of LiF/Li and LaF₃/La are calculated as shown in Table 1 based on the database in Outotec HSC Chemistry 6.0 [18] and thermodynamic calculation method reported before [19]. The table indicates that the standard potential of LaF₃/La is close to that of LiF/Li and this may lead to the deposition of Li when extracting La from molten fluoride salts. Lanthanum is found to predominantly exist in the species of LaF₆³⁻ instead of La³⁺ in LaF₃-KF [20] and NaF-LiF-LaF₃ [21] salts at the liquid states. The XRD analysis (Fig. 1) of the quenched LiF-KF-LaF₃ molten salt (2.73 wt% LaF₃ dissolved in eutectic LiF-KF molten salt) at room temperature in our study also indicates the existence of LaF₆³⁻. In that case, the redox reaction happens to La in LiF-KF-LaF₃ molten salt when K₃LaF₆ is formed, for example, would be



Comparing with the redox reaction of LaF₃/La, the standard reduction potential $E_{\text{K}_3\text{LaF}_6/\text{La}}^\circ$ for redox reaction K₃LaF₆/La can be expressed by

$$E_{\text{K}_3\text{LaF}_6/\text{La}}^\circ = E_{\text{LaF}_3/\text{La}}^\circ + \frac{\Delta G(\text{K}_3\text{LaF}_6)}{nF} \quad (5)$$

where $\Delta G(\text{K}_3\text{LaF}_6) = G(\text{K}_3\text{LaF}_6) - 3G(\text{KF}) - G(\text{LaF}_3)$, $E_{\text{LaF}_3/\text{La}}^\circ$ is the standard reduction potential for redox reaction LaF₃/La. Providing the value on $\Delta G(\text{K}_3\text{LaF}_6)$ which is reported as 295 kJ/mol in the previous literature [22], the electrodeposition potential for La will shift

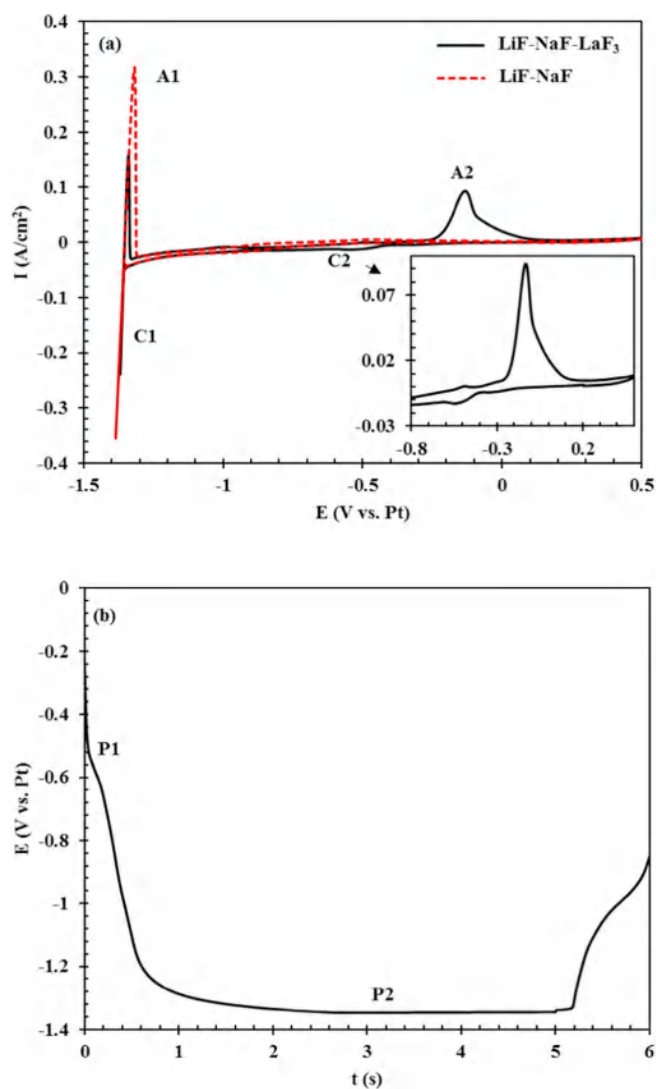


Fig. 5. (a) Cyclic voltammograms obtained in LiF-NaF eutectic molten salt with LaF_3 dissolved in and pure LiF-NaF eutectic molten salt at the scan rate of 200 mV/s. Inset photograph: the enlargement of the CV curve obtained in LiF-NaF- LaF_3 salt; (b) Chronopotentiogram of the system of LiF-NaF- LaF_3 with the applied current of -20 mA (working electrode area = 0.577 cm 2). Working electrode: Mo; counter electrode: graphite; LaF_3 = 3.02 wt%; T = 1023 K.

positively by 1.02 V.

Based on the discussion above, the presence of KF or NaF will result in the formation of LaF_6^{3-} and the electrodeposition of La in its metal form from molten fluoride salts will be much easier. The electrochemical behaviors of La in molten LiF, LiF with the addition of KF, and LiF with the addition of NaF will be investigated to confirm our theory, respectively. Comparing with the electrodeposition methods assisted by the liquid electrode and solid reactive electrode, the previously discussed challenges no longer persist if this new method is used. More importantly, no additional separation of the deposited metal from the liquid electrode or the formed metallic compounds is needed, which will greatly reduce the separation costs.

2. Experimental

All of the experiments and sample preparations in this study were performed inside a glove box (PureLab HE, Innovative Technologies) with an argon atmosphere ($\text{O}_2 < 5$ ppm, $\text{H}_2\text{O} < 0.1$ ppm). Reagents used for this work include lithium fluoride (> 99.0% purity, Sigma

Aldrich), sodium fluoride (> 99.0% purity, Sigma Aldrich), potassium fluoride (> 99.5% purity, Sigma Aldrich), and lanthanum fluoride (99.99% purity, Sigma Aldrich). The salts are weighed by a precision balance with an accuracy of 0.0001 g (MS 105DU Mettler Toledo). The weighed salt was mixed well before being transferred to a nickel crucible (Sigma Aldrich) and placed in a muffle furnace (ThermoFisher Scientific FB1315M) for which the temperature can be maintained within $\pm 1^\circ\text{C}$ during the experiment. The salt mixture was dehydrated at 473 K for 24 h before heating to the target temperature. The electrochemical tests were carried out by a potentiostat (Gamry Interface 1000) and a standard three-electrode setup. The working electrode used was a 3.17 mm diameter molybdenum rod (99.95% purity, Alfa Aesar). The counter electrode was a 3.05 mm diameter graphite rod (99.9995% purity, Alfa Aesar). The reference electrode utilized was a 0.81 mm diameter platinum wire (Surepure Chemetals). The surface area of the working electrode was measured according to the submerged depth into the salt melt. For all the electrochemical tests, IR compensation that programmed in Gamry Framework software was selected to remove the effect of IR correction on the shape and magnitude of cyclic voltammogram and chronopotentiogram.

To get the cathode depositions, electrolysis was performed on the working electrode. The working electrode after electrolysis was taken out from molten salt immediately and sealed inside epoxy to make SEM (scanning electron microscopy) sample. The sample was polished using SiC sandpaper and then the cross-section of the working electrode in the prepared SEM sample was characterized by scanning electron microscopy (SEM, FEI Quantan 600) to examine the composition and morphology.

3. Results and discussions

The typical cyclic voltammograms of LiF and LiF- LaF_3 recorded on Mo working electrode are shown in Fig. 2. The result obtained in pure LiF shows no obvious peak in the sweep range between -1.7 V and 0.5 V (vs. Pt), proving the absence of electrochemical reactions. The sharpness of the reduction current at -1.7 V (vs. Pt) should be attributed to the reduction of Li (I). In addition to the redox peaks of Li (I)/Li, the cyclic voltammogram shows a new pair of redox peaks when LaF_3 was dissolved in molten LiF salt, which should be attributed to the reaction of $\text{La (III)} \leftrightarrow \text{La}$ [23]. The cyclic voltammetry result obtained on inert Mo electrode also indicates that the electrodeposition of La metal proceeds just prior to the solvent reaction (Li (I)/Li), which is in accordance with thermodynamic calculation in Table 1. In the molten LiF, the co-electrodeposition of La and Li may occur when the concentration of La^{3+} ions are at a relatively low level, which means that it is difficult to separate trace amounts of species La^{3+} from the molten LiF salt. Considering the low concentration of lanthanum impurity in molten salt reactor coolant, it is highly possible that La and Li will co-electrodeposit by merely using an inert electrode. To make the electrodeposition of La easier, Ambrová et al. [23] applied solid Ni as the reactive working electrode through which the metallic compounds between La and Ni were formed on this electrode.

Considering the isolation of the formed metallic compound on the reactive solid electrode, one must find a new way to extract lanthanum from molten salts. As calculated in Table 1, with the addition of either KF or NaF into molten LiF, the formation of K_3LaF_6 (or Na_3LaF_6) allows the electrodeposition of La proceed at a considerably more positive potential [20,21]. To verify this prediction, the electrochemical tests were carried out in the LiF- LaF_3 molten salt system with KF added and the results are shown in Fig. 3. The cyclic voltammogram curve obtained in the eutectic LiF-KF (Fig. 3a, dashed line) illustrates no redox peak in the potential range from -1.4 V to 0.4 V (vs. Pt). According to the standard reduction potential shown in Table 1, the reduction of K(I) is easier to occur than that of Li (I) in fluoride salts. Thus, the cathodic and anodic limit C1 and A1 at the left side of the electrochemical window should be attributed to the redox reaction of K (I)/K. A new

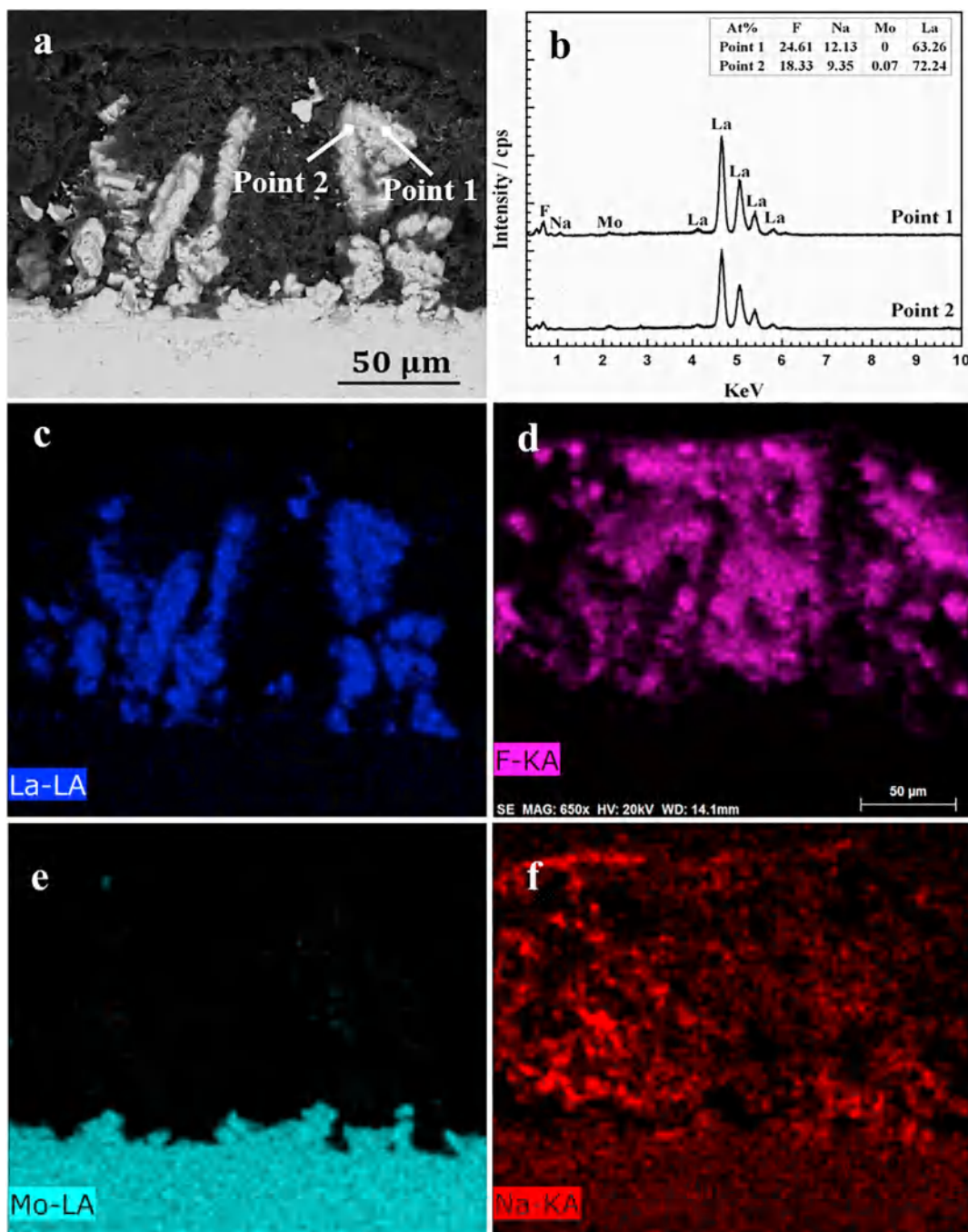


Fig. 6. (a) Backscattered electrons (BSE) image of the cross-section of polished Mo rod electrode after electrolysis in LiF-NaF-LaF₃ molten salt; (b) EDS point scan results of point 1 and point 2 in Fig. 6a; (c)-(f) EDS mapping results of Fig. 6a.

reduction peak C2 at -0.75 V (vs. Pt) appears after the addition of LaF₃ (Fig. 3a, solid line) which should be attributed to the electrodeposition of La. Comparing with the electrodeposition potential of La in LiF-LaF₃ shown in Fig. 2, the positive shift on potential caused by the addition of KF is about 1.0 V, which is in good agreement with the calculated results in Table 1. In addition to the cyclic voltammetry test, the chronopotentiometry was performed, the plateau P1 in the obtained chronopotentiogram shown in Fig. 3b also indicates a great positive shift on the electrodeposition potential of La after KF was added in.

To further confirm the electrodeposition of La, A stable current of -4 mA was provided for 1800s on a Mo working electrode to do chronopotentiometry electrolysis in the LiF-KF eutectic molten salt with 2.73 wt% LaF₃ dissolved in. The cathode potential was monitored and

controlled to not reach the reduction potential of alkali species during the electrolysis process. The Mo electrode was taken out from the electrochemical cell immediately after chronopotentiometry electrolysis for subsequent SEM analysis. Fig. 4 shows the SEM results of the cross-section of the polished Mo rod electrode after chronopotentiometry electrolysis. The backscattered electrons (BSE) image is shown in Fig. 4a in which the grey bottom part and the top black part are Mo electrode and solidified salt, respectively. Plenty of La was accumulated after electrolysis, which can be seen in the middle of the image as shown in Fig. 4(a). The point scans of the La-rich part show the signal for La element is very strong while it is extremely weak for the element of F. It means the substance deposited is La metal. Fig. 4 (c-f) shows the EDS mapping results from which the absence of F at the

place where La is concentrated can be observed and it further confirms that the deposited material after chronopotentiometry electrolysis is La metal. Therefore, the addition of KF assists the extraction of La from molten LiF salt and makes it occur at a more positive potential.

Similarly, electrochemical tests were also carried out in LiF-LaF₃ molten salt system with the addition of NaF. Fig. 5 shows the cyclic voltammogram and chronopotentiogram obtained on Mo working electrode in the LiF-NaF-LaF₃ molten salt system. Based on the calculation in Table 1, the peak C1 in the CV test (Fig. 5a) and P2 in chronopotentiometry test (Fig. 5b) should be attributed to the reduction of Na (I). With the addition of NaF, a pair of redox peaks (peak C2 and A2) was observed in just the way that the electrochemical behavior of the system was recorded when KF was added. The reduction peak of C2 should be the electrodeposition of La metal while the oxidation peak A2 is the oxidation process of the deposited La. Also, a plateau P1 in (Fig. 5 (b)) can be seen, which should be related to the deposition of La metal. The same process was conducted as done in the LiF-KF-LaF₃ system in which a stable current of -4 mA was applied on the Mo rod electrode for 1800s to do chronopotentiometry electrolysis in the LiF-NaF-eutectic molten salt with 3.02 wt% LaF₃ dissolved in. Then the Mo rod electrode was polished and an SEM test was performed on its cross-section. Fig. 6 shows the obtained SEM results. It can be identified that the element of F rarely exists in the La-rich locations, which indicates the product produced by the electrolysis is La metal. A strong signal of La can also be observed in the point scans of La concentrated part. Some amounts of F were also found in the point scans which could be attributed to the salt stuck to the La metal surface. Combining the electrochemistry and SEM test results, it can be concluded that the extraction of La in molten LiF salt can also be assisted by the addition of NaF.

4. Conclusion

The present study investigated a new method of reducing La ions in molten fluoride salt to La metal. In this new method, KF or NaF is added into the molten fluoride salt in which La predominantly exists in the form of LaF₆³⁻ instead of La³⁺ species and then the equilibrium reduction potential of La shifts to a more positive value. Unlike electrodeposition methods assisted by using liquid metal and reactive electrodes, which face the challenges of the isolation of the reactive electrode due to the formation of intermediate compound and the ability to maintain a low activity value of active metal in liquid electrode, the method developed in the study will help get pure La metal in a simpler way. It is anticipated that this technique can also be applied to extract other active metals such as critical materials (rare earth metals) from molten fluoride salts or other kinds of molten salt systems.

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