

# Electrochemical Co-reduction of Bi(III) and Y(III) and Extracting Yttrium from Molten LiCl-KCl Using Liquid Bi as Cathode

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**Abstract** The electrochemical reaction of Bi(III) and co-reduction behaviour of Bi(III) and Y(III) ions were researched in molten LiCl-KCl on a tungsten(W) electrode employing a range of electrochemical techniques. Cyclic voltammetric and square-wave voltammetric results revealed that the reduction of Bi(III) was a one-step process, with the exchange of three electrons on a W electrode, and diffusion-controlled. The electrochemical curves showed two reduction peaks pertaining to the formation of Bi-Y alloy compounds, because of the co-reduction of Bi(III) and Y(III) by metallic Y deposited on the pre-deposited Bi-coated W electrode and reacting with Bi metal in molten LiCl-KCl. Furthermore, galvanostatic electrolysis was conducted using liquid Bi as cathode to extract yttrium at different current intensities, and the extractive products were analyzed by SEM, EDS and XRD. The results indicated that BiY intermetallic compound was formed in the molten LiCl-KCl-YCl<sub>3</sub> system.

**Keywords** Electrochemical co-reduction; Electrochemical behaviour; Bi-Y intermetallic compound; Galvanostatic electrolysis

## 1 Introduction

Nuclear energy plays a significant role in developing new energy. However, the management of spent nuclear fuels in a mode of safety and economy has become one of the most essential issues correlated to the sustainable development of nuclear energy production. Thus, the recovery of actinides(Ans) from fission products has become a priority for nations using nuclear energy. In recent years, partitioning and transmutation have been extensively explored to extract Ans(uranium, plutonium) and minor actinides from spent nuclear fuels<sup>[1–3]</sup>.

Pyrochemical processes with irradiation tolerant can be used to process spent fuel with deep burn-up and short cooling-off periods<sup>[4–6]</sup>, and is considered the key link in developing fast-reactor and accelerator-driven sub-critical transmutation technology. They include mainly fluoride volatility<sup>[7]</sup>, electrorefining<sup>[8,9]</sup>, molten salt-liquid metal reductive extraction<sup>[10]</sup> and electrochemical extraction using reactive cathodes<sup>[11,12]</sup>.

Bismuth metal, having a low melting point, is considered a good candidate for reactive electrodes. Because alloying of Bi with rare earths(REs) is easy and fast, some researchers have investigated the electroextraction of REs from LiCl-KCl melts.

Castrillejo *et al.*<sup>[13,14]</sup> researched the electrochemical behaviours of Ce(III) and Pr(III) on Bi-coated W electrodes, employing various electrochemical techniques, and estimated the thermodynamic data of the formation of Ce-Bi and Pr-Bi intermetallic compounds using electromotive force(EMF). Jiang *et al.*<sup>[15]</sup> investigated the electrochemical reaction of Pr(III) on Bi film electrodes in molten LiCl-KCl, and two kinds of Pr-Bi intermetallics, PrBi<sub>2</sub> and PrBi, were obtained using a liquid Bi pool electrode. The co-reduction behaviours of Bi(III) and RE(III) (RE = La, Tb, Dy, Ho) were explored by our group<sup>[16–19]</sup>, and different Bi-RE(RE = La, Tb, Dy, Ho) alloys were extracted on liquid Bi electrodes. The thermodynamic properties for Bi-RE (RE = La, Tb, Dy, Ho) intermetallics were also calculated in molten LiCl-KCl by EMF.

However, electrochemical extraction of yttrium has not been researched on liquid Bi cathode in molten LiCl-KCl. To gain the basic electrochemical information of Y(III) on liquid Bi electrode, the co-reduction of Bi(III) and Y(III) was studied by a sequence of electrochemical methods. Furthermore, the extraction of yttrium was also conducted using liquid Bi as cathode, and the products were investigated by SEM-EDS and XRD.

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## 2 Experimental

### 2.1 Electrochemical Apparatus and Electrodes

Electrochemical tests and sample preparation were carried out in an argon-atmosphere glove box (<5  $\mu\text{L/L}$   $\text{O}_2$  and  $\text{H}_2\text{O}$ ). A three-electrode system was established. A silver wire (1 mm diameter, purity 99.95%) was dipped into eutectic LiCl-KCl containing 1.0% (mass fraction) AgCl (purity 99.99%), which was placed into a Pyrex tube. Tungsten wire with a diameter of 1.0 mm was served as working electrode, whose surface was polished with sandpaper, and washed with distilled water and alcohol, respectively. After each electrochemical test, the active electrode area was measured by determining the immersed depth of the working electrode in the molten salts. A liquid Bi electrode was chosen as working electrode to explore the electrochemical preparation of Bi-Y alloys. The liquid Bi electrode was composed of a pool of liquid Bi (purity 99.99%) in an alumina tube. A W wire (1 mm diameter, purity 99.9%) was used for electrical connections. Spectrally pure graphite rod (6.0 mm diameter) was chosen as the counter electrode. A Metrohm electrochemical workstation (Autolab PGSTAT302N) with electrochemical software (NOVA 1.10) was employed to perform the electrochemical measurements.

### 2.2 Melt Preparation

Anhydrous LiCl and KCl (purity >99.95%) were purchased from Xilong Chemical Reagent Co., Ltd. (Shantou, China). LiCl-KCl (45.8:54.2, mass ratio) was mixed in an alumina crucible and dried at 573 K for more than 20 h in order to remove the residual water. The metal ion impurities in molten LiCl-KCl were removed by pre-electrolysis conducted at  $-2.1$  V (vs. Ag/AgCl) for 6 h. Anhydrous  $\text{BiCl}_3$  (purity >99.9%; Yunyang New Materials Co., Ltd., Shanghai, China) and  $\text{YCl}_3$  (purity >99.9%; Jining Zhongkai New Materials Co., Ltd., Jining, China) were added to the eutectic melts, respectively.

### 2.3 Analysis Techniques

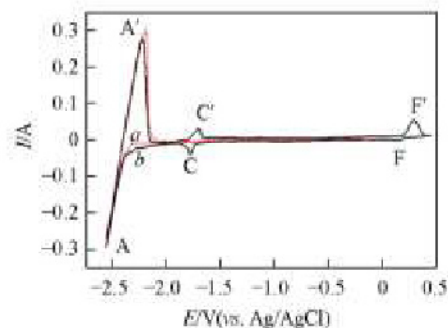
X-Ray diffraction instrument (XRD, Philips, Netherlands) was used for qualitative measurements and phase analysis of the extraction products and scanning electron microscopy coupled with energy dispersive spectrometry (SEM-ED,

HITACHI SU-70, Japan) was applied to identify the morphology and micro-zone chemical analysis of Bi-Y alloys.

## 3 Results and Discussion

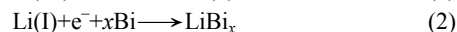
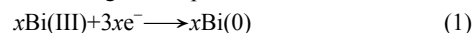
### 3.1 Electrochemical Behaviour of Bi(III) on an Inert W Electrode

Cyclic voltammetry (CV) was carried out in molten LiCl-KCl and LiCl-KCl- $\text{BiCl}_3$  (0.12%) systems, and the results are shown in Fig. 1. In molten LiCl-KCl (curve *a*), a pair of signals of A/A' pertains to the reduction and dissolution of Li metal. In addition to the A/A' signals, two pairs of cathodic/anodic signals (C/C' and F/F') are detected at approximately  $-1.78/-1.69$  V and  $0.16/0.29$  V (curve *b*), respectively. The redox couple of F/F' has been exhaustively studied by other authors<sup>[16-19]</sup>, and is associated with the Bi(III)/Bi(0) couple.

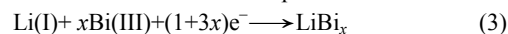


**Fig.1** Cyclic voltammograms recorded in molten LiCl-KCl before (*a*) and after (*b*) the addition of  $\text{BiCl}_3$  (0.12%) on W electrode ( $S=0.322$   $\text{cm}^2$ ) at 773 K and a scan rate of 0.1 V/s

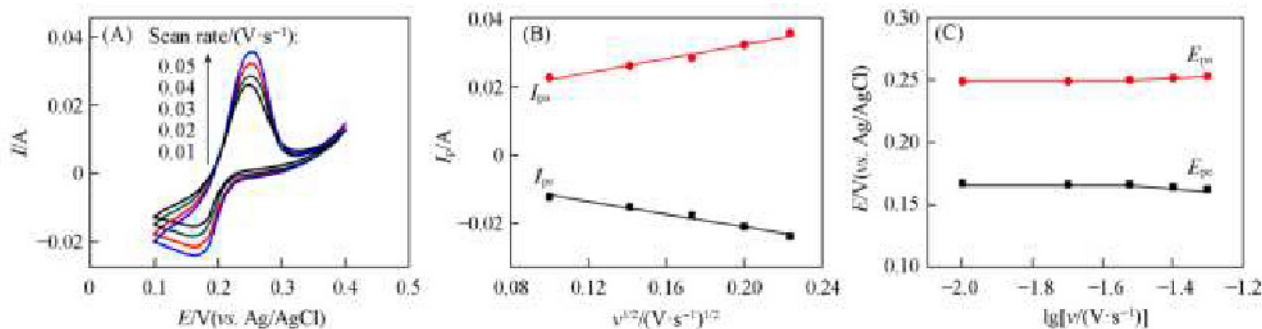
The redox signals C/C', detected between the signals A/A' and F/F', pertain to the formation/re-dissolution of Bi-Li alloy. The formation process of the Bi-Li intermetallic compound is expressed by the following two steps:



The formation of the  $\text{LiBi}_x$  intermetallic compound was resulted from metallic Li depositing on the pre-deposited Bi electrode. The overall reaction can be expressed as follows:



CV was conducted in LiCl-KCl- $\text{BiCl}_3$  (0.12%) melts at scan rates of 0.01–0.05 V/s, as shown in Fig. 2(A). The



**Fig.2** Cyclic voltammograms recorded in molten LiCl-KCl- $\text{BiCl}_3$  system at 773 K on W electrode ( $S=0.322$   $\text{cm}^2$ ) at different scan rates (A), plots of anodic and cathodic peak currents as a function of square root of scan rates (B) and plots of anodic and cathodic peak potentials vs. logarithm of scan rates (C)

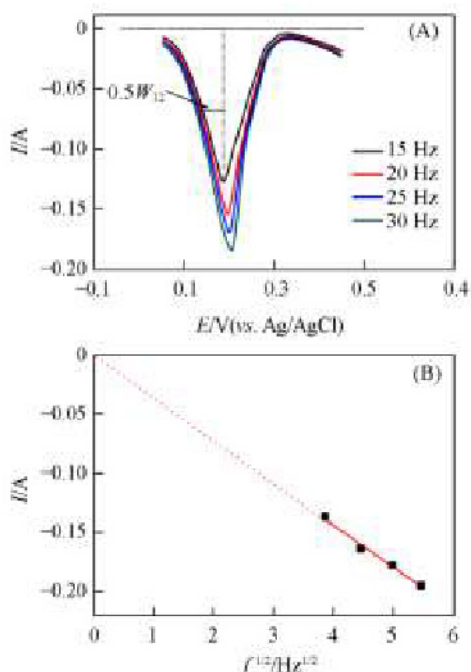
cathodic/anodic peak currents increase with the increase in scan rates. The linear relationship between peak currents ( $I_{pc}$  and  $I_{pa}$ ) and the square root of the scan rates can be seen in Fig.2(B), which indicates that the reduction of Bi(III) is a simple diffusion-controlled process, while the peak potentials ( $E_{pc}$  and  $E_{pa}$ ) shift towards the cathodic and anodic direction with the logarithm of the scan rates [Fig.2(C)]. Thus, we suggest that the reduction of Bi(III) ion on the W electrode is a diffusion-controlled but not reversible process.

Square-wave voltammetry (SWV) was applied to calculate the number of exchange electrons in the electrochemical process by the following equation, in which the width  $W_{1/2}$  of the peak at half height is dependent on the number of electrons transferred ( $n$ ) and temperature ( $T$ )<sup>[20,21]</sup>:

$$W_{1/2} = 3.52RT/nF \quad (4)$$

where  $R$  ( $J \cdot mol^{-1} \cdot K^{-1}$ ) is the ideal gas constant, and  $F$  (C/mol) represents the Faraday constant.

Fig.3(A) displays the series of square-wave voltammograms of Bi(III) acquired on the W electrode at different frequencies. We can observe a linear relationship of peak current with the square root of the frequency, and the intercept is nearly zero, as shown in Fig.3(B). Thus, according to Eq.(4), the calculated average value of  $n$  is 2.73, close to 3.0, which reveals that the reduction of Bi(III) to Bi metal proceeds in one step with the exchange of three electrons.



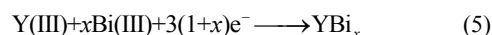
**Fig.3** Square-wave voltammograms of LiCl-KCl-BiCl<sub>3</sub> (0.12%) melts at different frequencies(A) and the plot of peak current vs. square root of frequency(B)

Working electrode: W ( $S = 0.322 \text{ cm}^2$ ); pulse amplitude: 0.025 V; potential step: 0.005 V.

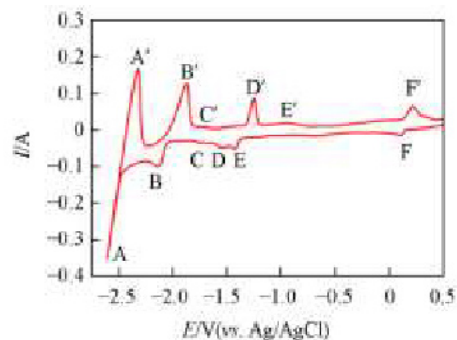
### 3.2 Electrochemical Co-reduction of Bi(III) and Y(III) in Molten LiCl-KCl

Fig.4 presents the cyclic voltammograms acquired in the molten LiCl-KCl-BiCl<sub>3</sub>(0.12%)-YCl<sub>3</sub>(2.4%) system. A range of

redox peaks are detected. Aside from the signals of A/A', C/C' and F/F' mentioned above, the signals of B/B' recorded at  $-2.14/-1.87 \text{ V}$  pertain to the formation/re-dissolution of Y metal. Two peaks D and E, detected at  $-1.55$  and  $-1.42 \text{ V}$ , pertain to the formation of two Bi-Y alloy compounds. The formation process is expressed by the following two reactions:  $x\text{Bi(III)} + 3xe^- \rightarrow x\text{Bi(0)}$  and  $\text{Y(III)} + 3e^- + x\text{Bi} \rightarrow \text{YBi}_x$ . The formation of the intermetallic compound  $\text{YBi}_x$  was resulted from the metallic Y depositing on the pre-deposited Bi electrode. The overall process is expressed by the following reaction:



It is obvious that a depolarisation effect of Y(III) reduction can be observed on the pre-deposited Bi electrode because of the formation of Bi-Y alloys by co-reduction of Bi(III) and Y(III) ions.

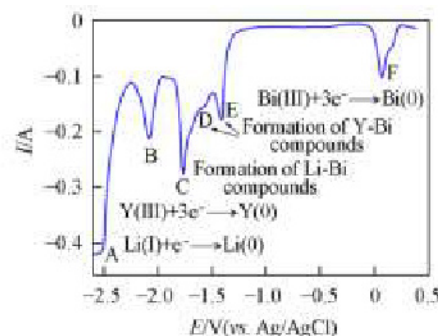


**Fig.4** Cyclic voltammogram recorded on W electrode in LiCl-KCl-BiCl<sub>3</sub>-YCl<sub>3</sub> melt

Scan rate: 0.1 V/s;  $S = 0.322 \text{ cm}^2$ .

SWV has a higher sensitivity and resolution than CV<sup>[22-24]</sup>. For further research into the electrochemical co-reduction of Bi(III) and Y(III) on a W electrode, SWV was employed to study the co-reduction of Bi(III) and Y(III) in molten LiCl-KCl-BiCl<sub>3</sub>(0.12%)-YCl<sub>3</sub>(2.4%) system on a W electrode. Six reduction peaks are detected in the SWV curve in Fig.5. Apart from current signals of A, B and F related to the deposition of metallic Li, Y and Bi, respectively, cathodic peaks C, D and E, identified at  $-1.76$ ,  $-1.56$  and  $-1.49 \text{ V}$ , are related to the formation of different Bi-Li and Bi-Y intermetallics, respectively. The results are in good agreement with those obtained by CV (Fig.4).

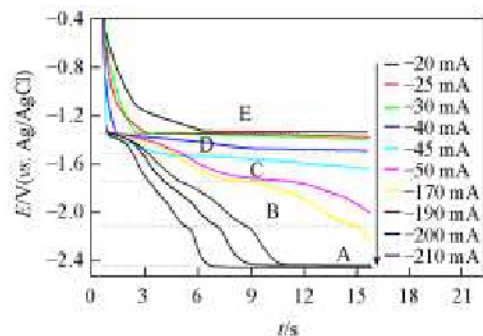
Fig.6 demonstrates the chronopotentiograms recorded on



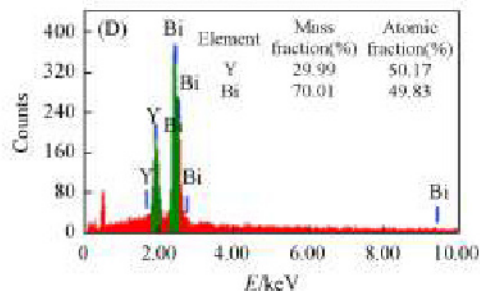
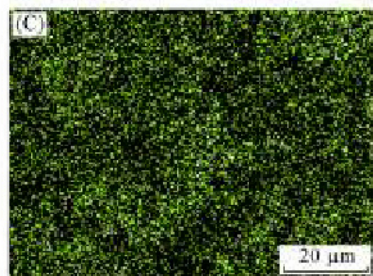
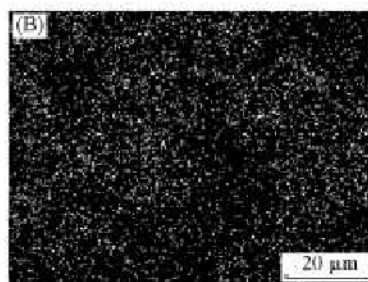
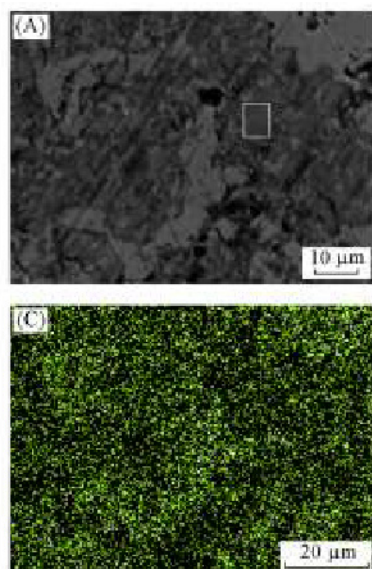
**Fig.5** Square wave voltammogram obtained in the molten LiCl-KCl-BiCl<sub>3</sub>-YCl<sub>3</sub> system on the W electrode ( $S = 0.322 \text{ cm}^2$ ) at 773 K

Potential step: 1 mV; frequency: 20 Hz.

a W electrode at various current intensities in molten LiCl-KCl-BiCl<sub>3</sub>(0.12%)-YCl<sub>3</sub>(2.4%) system at 773 K. Five potential plateaus are observed in the chronopotentiograms. The first plateau E occurs at -1.35 V, when the applied current intensity is more positive than -30 mA, and is related to the formation of Bi-Y intermetallics on the W electrode. When the current intensity reaches -40 mA, the second plateau D is detected at -1.50 V, which is correlated with another Bi-Y



**Fig.6** Chronopotentiograms gained in molten LiCl-KCl-BiCl<sub>3</sub>(0.12%)-YCl<sub>3</sub>(2.4%) system on the W electrode ( $S=0.322 \text{ cm}^2$ ) at different current intensities



**Fig.7** SEM image(A), EDS mapping analysis[(B) and (C)] and EDS point analysis of the extractive obtained by galvanostatic electrolysis for 8 h at -0.5 A on a liquid Bi electrode ( $S=3.05 \text{ cm}^2$ ) at 773 K (B) Y; (C) Bi.

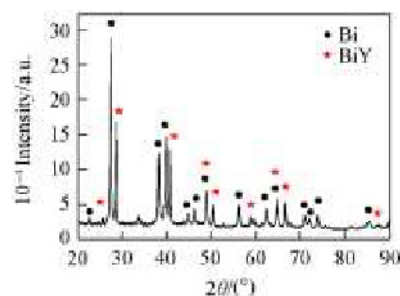
Fig.8 shows the XRD result of the Bi-Y alloy gained on a liquid Bi electrode by galvanostatic electrolysis at -0.5 A in the molten LiCl-KCl-YCl<sub>3</sub> system. It is clear that the Bi-Y intermetallic compound was formed in the Bi-Y alloy. The result is in agreement with that obtained by EDS analysis.

Fig.9(A) illustrates the SEM image of the extractive gained using galvanostatic electrolysis at -0.1 A in molten LiCl-KCl-YCl<sub>3</sub>(7.8%) systems on a liquid Bi electrode. From the EDS analysis, the Bi-Y alloy is composed mainly of Y and Bi elements[shown in Fig.9(B) and (C)], and the EDS result of the black-framed area in Fig.9(A) shows that the atomic ratio of Bi to Y is almost 1:1[Fig.9(D)].

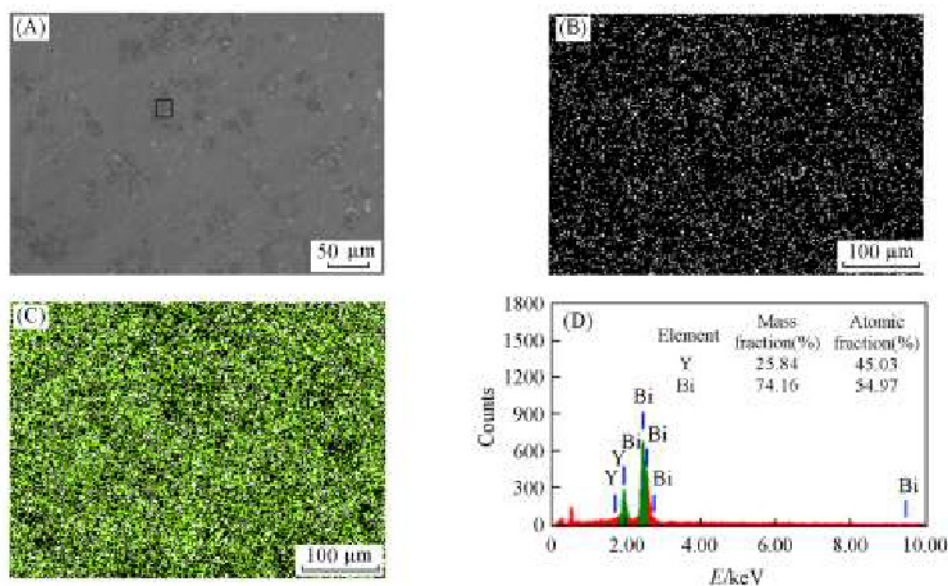
intermetallic compound. The third plateau, observed at -1.75 V, pertains to the co-reduction of Bi(III) and Li(I) when the currents are more negative than -50 mA. The fourth and the fifth plateaus, observed at -2.12 and -2.44 V, are correlated with the deposition of Y and Li metals, respectively, when the applied current reaches -200 mA. It is found that the reduction potentials gained by chronopotentiometry are in accordance with those acquired by CV and SWV.

### 3.3 Electrochemical Extraction and Characterization of Bi-Y Alloys

In order to electrochemically extract and prepare Bi-Y alloys, galvanostatic electrolysis experiments were conducted based on the results obtained by CV, SWV and chronopotentiometry on liquid Bi electrode in molten LiCl-KCl-YCl<sub>3</sub>(7.8%) systems. Fig.7(A) demonstrates the SEM image of the extractive obtained by galvanostatic electrolysis at -0.5 A on a liquid Bi electrode. There are two different zones seen in Fig.7(A). In order to confirm the distributions of metallic Bi and Y in the Bi-Y alloy, the results of EDS are shown in Fig.7(B) and (C). It is obvious that the Bi-Y alloy consists of Bi and Y elements, and the atomic ratio of Y to Bi is almost 1:1[Fig.7(D)].



**Fig.8** XRD pattern of the extractive obtained by galvanostatic electrolysis at -0.5 A for 8 h at 773 K on a liquid Bi electrode ( $S=3.05 \text{ cm}^2$ )



**Fig.9** SEM image(A), EDS mapping analysis[(B) and (C)] and EDS point analysis of the sample obtained by galvanostatic electrolysis at  $-0.1$  A for 3 h on a liquid Bi electrode ( $S = 3.05$  cm<sup>2</sup>) at 773 K (B) Y; (C) Bi.

## 4 Conclusions

The electrochemical co-reduction of Bi(III) and Y(III) on a W electrode in a molten LiCl-KCl-BiCl<sub>3</sub>-YCl<sub>3</sub> system was studied using a sequence of electrochemical techniques: CV, SWV and chronopotentiometry. The electrochemical signals corresponding to the formation of one Bi-Li and two Bi-Y alloy compounds were detected in the molten LiCl-KCl-BiCl<sub>3</sub>-YCl<sub>3</sub> system, because the metallic Li and Y could deposit on the pre-deposited Bi metal. Galvanostatic electrolysis was employed to extract yttrium on the liquid Bi electrode. The extractive products were analysed by SEM-EDS and XRD, which revealed the formation of BiY intermetallic compound.

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