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Electrochemical intercalation of potassium into graphite in KF melt

Dongren Liu[a,c], Zhanhong Yang[a,*], Wangxing Li[b], Shilin Qiu[b], Yingtao Luo[b]

[a] *College of Chemistry and Chemical Engineering, Central South University, South Lushan Road, Changsha 410083, Hunan, PR China*
[b] *Zhengzhou Research Institute of Chalco, Zhengzhou 450041, Henan, PR China*
[c] *Department of Chemical and Environmental engineering, Jiaozuo University, JiaoZuo 454003, Henan, PR China*

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ABSTRACT

Electrochemical intercalation of potassium into graphite in molten potassium fluoride at 1163 K was investigated by means of cyclic voltammetry, galvanostatic electrolysis and open-circuit potential measurements. It was found that potassium intercalated into graphite solely between graphite layers. In addition, the intercalation compound formed in graphite bulk in molten KF was quite unstable and decomposed very fast. X-ray diffraction measurements indicate that a very dilute potassium–graphite intercalation compound was formed in graphite matrix in the fluoride melt. Analysis with scanning electron microscope and transmission electron microscope shows that graphite was exfoliated to sheets and tubes due to lattice expansion caused by intercalation of potassium in molten KF.

1. Introduction

Aluminum is conventionally manufactured by Hall-Héroult electrolysis process at high temperature (around 1233 K). Carbon anodes are consumed and carbon dioxide is emitted during the process. It is a challenge for the aluminum industry worldwide to replace the carbon anode with inert anode so as to avoid consumption of carbonous materials, and most importantly, to eliminate the emission of greenhouse gas. Research on inert anodes for aluminum electrolysis has been carried out for several decades. However, only limited progress has been made in this field because the inert anodes are severely eroded by the high-temperature melts in the conventional Hall-Héroult process [1,2]. Low temperature electrolytes, especially those with a melting point below 1023 K, could increase the probability of finding a suitable inert anode material because the corrosion rate of inert anode would greatly be reduced at low temperature [3–5].

As compared with the NaF–AlF_3 system, the KF–AlF_3 system seems to be a promising candidate as low temperature electrolyte due to its lower eutectic temperature and higher alumina solubility. The eutectic temperature of KF–AlF_3 system is around 833 K while that of NaF–AlF_3 system is around 971 K [6]. The studies on KF–AlF_3-based electrolyte system were mainly focused on its physical or chemical properties and corrosion effects on inert anodes [6–9]. Penetration of the electrolyte into the cathode carbon block, however, is important since it affects the cell life in aluminum reduction cell. Although the inert cathode materials (wettable cathode) in which TiB_2 is the main component in either pure form or composite could be applied to a carbon lining, which may help to reduce the melt penetration and prolong cathode lifetime in the industrial cell [10], better understanding of potassium interaction with cathodic carbon block would be of basic importance to predict the performance of cathode when KF–AlF_3 system is used as low temperature electrolyte.

It has been found that potassium could intercalate into graphite lattice to form potassium–graphite intercalation compounds (K-GICs) with various stage structure either at relatively low temperature or in organic solutions [11–14]. However, it may not be the case for intercalation occurring between potassium and carbon in molten fluoride salt. Electrochemical intercalation of alkaline metals such as lithium and sodium into graphite in molten chloride has been employed to produce nano-sized carbon materials like tubes and particles [15–18]. Also, the intercalation of potassium into graphite by electrolysis in chloride melt has been reported and investigated for the mechanism in order to elucidate the role of potassium intercalation in the formation process of nano-sized carbon materials [19,20]. In the present work, the basic mechanism of potassium intercalation into graphite in the pure KF melt under cathodic polarization condition was discussed, with the aim of understanding the electrochemical intercalation process of potassium and the nature of the intercalation resultants.

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[*] Corresponding author. Tel.: +86 731 8836618; fax: +86 731 8879616.
E-mail address: zhyang@mail.csu.edu.cn (Z. Yang).

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2. Experimental

Anhydrous potassium fluoride contained in a graphite crucible was heated up to 523 K and held at this temperature for 8 h under vacuum, then heated up to the working temperature 1163 K, which is higher than the melting point of KF (1131 K). Electrochemical experiments were performed with a three-terminal electrochemical cell. The graphite crucible served as the container for the electrolyte and also as the high surface counter electrode. The working electrode (WE) was a thin sheet (with a dimension of 5.9 mm wide × 4 mm high × 1.2 mm thick exposed to molten salt) machined from a spectral pure graphite rod (d_{002} = 0.337 nm, crystallite size along c-axis L_c = 69 nm, apparent density = 1.78 g cm^{-2}, open porosity = 20.9%). The rest of graphite rod was shielded with BN tube. A stainless steel rod was connected to the graphite rod as current lead. Due to the difficulty of finding a suitable reference electrode in molten KF, platinum wire of 1.0 mm diameter was employed as the quasi-reference electrode. Hence, all potentials in the present work are expressed versus the platinum reference electrode. The stability of the quasi-reference electrode was confirmed by measuring the potential difference between two platinum wires in molten potassium fluoride for 12 h. It was found that the potential fluctuation of Pt electrode did not exceed ±10 mV. The graphite crucible was placed inside a sintered corundum tube within a programmable vertical furnace. The electrochemical cell was under a continuous nitrogen circulation during the experiment. Electrochemical measurements were performed with a PAR Model 263A Potentiostat/Galvanostat monitored by a computer with commercial PowerSuit software.

At first, the WE was characterized by means of cyclic voltammetry. Around 70% of the measured solution resistance between the working and reference electrodes was compensated for all cyclic voltammetric measurements. Secondly, the WE was subjected to galvanostatic electrolysis. Once the current was shut down, the open-circuit potential (OCP) of the WE was traced. After OCP measurements, the electrode was removed from the melt and cooled down naturally in nitrogen atmosphere. The electrode was washed with distilled water to get rid of the solidified electrolyte on the electrode surface. Scanning electron microscope (SEM) performed on JSM-6360LV (JEOM) was utilized to investigate the surface morphology of the electrode. In another case, the electrode just undergone galvanostatic electrolysis was taken out of the melt immediately, then cooled down rapidly in nitrogen atmosphere to room temperature and transferred into a glove box filled with high purity nitrogen. The graphite sheet was ground to powder and sealed with polyethylene film for X-ray diffraction (XRD) measurements which were performed on X'Pert Pro diffractometer (PANalytical) with Cu Kα radiation. Finally, after conducting galvanostatic electrolysis, a thin upper layer of solidified electrolyte in the cooled down graphite crucible was sampled to a 50-ml beaker. Then 30 ml of distilled water was added to the beaker and sonicated for 10 min. The aqueous mixture was left to stand overnight. Samples collected from the surface of the aqueous mixture by a pipette were dripped onto a holey carbon coated copper grid and then dried thoroughly for transmission electron microscope (TEM) analysis which was performed on JEM-2100 (JEOM, 200 keV, capable of energy dispersive X-ray analysis).

3. Results and discussion

3.1. Cyclic voltammetry

Potassium is soluble in molten potassium fluoride [21]. Furthermore, as reported in ref. [20], considerable evaporation of potassium occurred in the process of cathodic polarization as the working temperature (1163 K) is higher than the boiling point of potassium (1032 K). The interference of these two factors with potassium intercalation into graphite may influence the magnitude of the current that is attributed solely to the latter process. In order to evaluate the disturbance amplitude of potassium dissolution and evaporation, cyclic voltammogram was recorded on platinum electrode in molten KF at a scan rate of 100 mV s^{-1} at 1163 K (Fig. 1). Platinum electrode was chosen to estimate the current density caused by potassium dissolution and evaporation due to its chemical inertness against potassium and fluoride melt. The voltammogram in Fig. 1 shows potassium deposits at the potential of ca. −1.1 V. It is notable that the oxidation peak of potassium is absent during the anodic scan even when the cathodic potential is down to −1.5 V. That strongly indicates that potassium deposited in cathodic process undergoes very rapid dissolution and evaporation. That is, metallic potassium generated at the cathodic sweep had completely escaped from the electrode surface before the sweep was reversed to its oxidation potential at the potential scan rate, which is in agreement with that reported by Chen et al. [20].

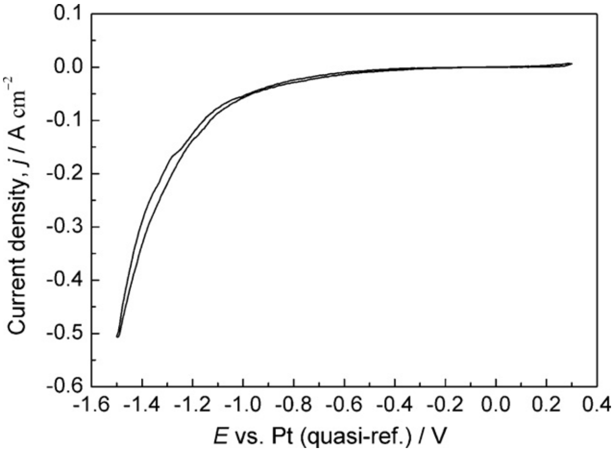

Fig. 1. Cyclic voltammogram recorded on platinum electrode in molten KF at 1163 K. Potential scan rate = 100 mV s^{-1}.

Fig. 2 presents cyclic voltammograms recorded on the platinum wire and the graphite sheet electrode in molten potassium fluoride at 1163 K. The potential was scanned from a potential at which no reduction or oxidation reaction occurred in the negative direction and switched at −1.1 V to avoid the deposition of metallic potassium at a scan rate of 100 mV s^{-1}. The cyclic voltammetric behavior of graphite differs greatly from that of platinum. A reduction wave starts from around −0.8 V on graphite electrode, and then the cur-

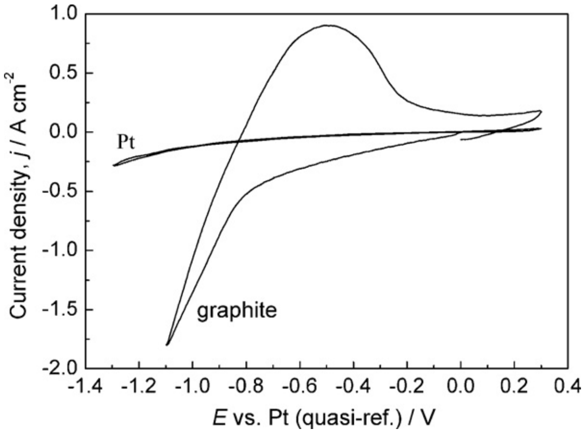

Fig. 2. Cyclic voltammograms recorded on graphite and platinum electrode in molten KF at 1163 K. Potential scan rate = 100 mV s^{-1}.