

Electrochemical investigation of the anode processes in LiF-NdF₃ melt at low oxygen content

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Abstract:

The oxidation of oxygen ions and the generation of anode effect at low oxygen content of 150 ppm were discussed in this paper. Cyclic voltammetry and square-wave voltammetry were used to explore the anodic processes of LiF-NdF₃ melt after a long period of pre-electrolysis purification at 1000°C (oxygen content reduces from 413 ppm to 150 ppm). The oxidation process of oxygen ions can be divided into two stages: the oxidation products adsorption and CO/CO₂ gas evolution stage. The adsorption stage is controlled by diffusion-controlled step, while the control process of gas evolution is electrochemical reaction step. At low oxygen content of 150 ppm, the decline amplitude of the current is much more gentle in the positive scan when anode effect occurs. The fluorine ions oxidation peaks at about 4.2 V (vs. Li/Li⁺) are clearly observed in the reverse scanning processes, at which the oxidation of fluorine ions and the production of perfluorocarbon occur resulting in anode effect.

KEYWORDS: LiF-NdF₃ melt; Nd electrowinning; Low oxygen content; Anode processes

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1 Introduction

Neodymium, as a very typical rare earth element, is widely used in the field of permanent magnet and non-ferrous metal modification [1-2]. The most significant method for producing neodymium metal is molten salts electrolysis, which is suitable for mass production due to a continuous operation process. Fluoride-oxide molten salts media is the most commonly used electrolyte system for the neodymium electrowinning in the modern industry because it has shown a lower hygroscopicity and higher current efficiency than chloride electrolytes [3-6]. However, in the Fluoride-oxide electrolysis processes, the graphite anode can cause serious problems due to formation of the perfluorocarbons (PFCs) and generation of the anode effect. Perfluorocarbons mainly composed of CF_4 and C_2F_6 are typical greenhouse gases, and their emission needs to be strictly controlled for environmental protection.

In order to eliminate the generation of PFCs, it is necessary to understand the mechanism of PFCs generation. The anode effect and PFCs generation of aluminium electrolysis conducted in molten fluoride salts have been ever studied by S.S. Nissen and D.R. Sadoway et.al. [7-9]. Even though aluminum electrolysis and neodymium electrolysis both carried out in fluoride molten salts, there is still a huge difference between their anode processes. The anode effect of neodymium electrolysis and the composition of the anode gases in LiF-NdF_3 melt have been explored by H. Zhu et.al. [6, 10]. Over the years, our laboratory has explored the anode processes for Nd electrowinning from $\text{LiF-NdF}_3\text{-Nd}_2\text{O}_3$ melt [11].

In this paper, the LiF-NdF_3 system was adopted to conduct long-term pre-electrolysis purification in order to reduce the oxygen content in the molten salts as much as possible, and the anode processes of neodymium electrolysis in the LiF-NdF_3 melt was studied under the condition of approaching pure fluoride. Cyclic

voltammetry and square-wave voltammetry were used to investigate the oxidation processes of oxygen ions and the potential of fluoride ions oxidation and PFCs generation in a pure fluoride system with very low oxygen content about 150 part per million (ppm).

2 Experimental

A sealed cylindrical stainless steel reactor with a stainless-steel lid was used in all electrochemical experiments in this paper. LiF (Hebei Yucheng Chemical Co., Ltd.) and NdF₃ (Xuzhou Jinshi Pengyuan Rare Earth Material Factory) were respectively maintained at 400 degrees Celsius (°C) for more than 12 hours (h) under vacuum to remove moisture and then mixed in the proportion of 30 percent weight (wt%) and 70wt% in a vacuum glove box. Well mixed LiF (60 grams) and NdF₃ (140 g) in the graphite crucible were continuously heated to 1000°C at a speed of 5 degrees Celsius per minute (°C/min) and kept for 2 h in an argon atmosphere. All the electrochemical experiments were conducted in a three-electrode system in argon atmosphere, in which a tungsten (W) wire with a diameter (Φ) of 1 millimeter (mm) was used as the quasi-reference electrode, and then the potential was transferred to Li/Li⁺ reference electrode by electrochemical measurements according to the literature [12]. A high purity graphite rod (Φ6 mm) and a molybdenum (Mo) wire (Φ0.8 mm) were used as the working and counter electrode, respectively.

Three electrodes were polished and placed into the LiF-NdF₃ melt then connected to a PAR-STAT2273 (PAR-Ametek Co, Ltd.) workstation with a PowerSuite software package for the testing of cyclic voltammetry (CV) and square wave voltammetry (SWV).

3 Results and discussion

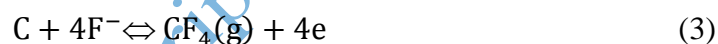
3.1 Cyclic voltammetry

Cyclic voltammetry was performed to record the electrochemical processes on a graphite anode in the molten LiF-NdF₃ (30wt%-70wt%) melt at 1000°C. Fig.1 (a) shows the cyclic voltammograms obtained by forward scanning from open-circuit potential to 5.5 voltage (V) (vs. Li/Li⁺) before (curve 1) and after (curve 2) 5 hours of pre-electrolysis purification. In curve 1, the oxidation current appears from 1.9 V (vs. Li/Li⁺) and peaks at 2.5 V (vs. Li/Li⁺) with a peak current density of 0.080 ampere per square centimeter (A/cm²), which has been confirmed in our previous experiments that it is produced by the oxidation of oxygen ions [11]. Despite a long period of drying and pre-melting treatments, the system still contains a certain amount of impurity oxygen ions (oxygen content: 413 ppm). After 5 hours of pre-electrolysis purification (oxygen content: 150 ppm), it can be clearly observed from Fig.1 (a) that the current density of curve 2 is significantly smaller than that before pre-electrolysis. The oxidation current appears from 2.3 V (vs. Li/Li⁺), which is more positive than curve 1, and the peak current density at 2.6 V (vs. Li/Li⁺) is smaller than that of curve 1 with a value of 0.025 A/cm², indicating a lower oxygen ion concentration in the melt after pre-electrolysis. It is obvious that the current of curve 1 is smooth before 2.75 V (vs. Li/Li⁺), then fluctuates sharply and rapidly increases to 0.38 A/cm² when the potential exceeds 2.75 V (vs. Li/Li⁺). It can be inferred that the smooth current curve is the adsorption process of substances produced by oxygen ion oxidation on the graphite anode as shown in formula (1) and (2), and the violent fluctuation in current curve 1 is caused by the release of anode gas including carbon monoxide (CO) and carbon dioxide (CO₂) [6, 9- 11].



Therefore, the oxidation of oxygen ions can be divided into two stages, the oxidation products adsorption and CO/CO₂ gas evolution stage, corresponding to the smooth current curve and the fluctuation current curve, respectively. In comparison with CV before pre-electrolysis, the CV after pre-electrolysis shows longer adsorption time and shorter fluctuation time due to lower oxygen ion content in the melt.

For the molten salts before pre-electrolysis, when the potential exceeds 4.5 V (vs. Li/Li⁺), the current drops sharply to a very low value of 0.025 A/cm², which is caused by the anode effect similar to the case in aluminum electrolysis [13]. This is due to the generation of a 'CF' film on the electrode surface to form an insulation state, which causes the anodic oxidation current to drop sharply to an extremely small degree [9, 14, 15]. The gas produced on a graphite electrode at potentials exceeding 4.5 V (vs. Li/Li⁺) was confirmed by H. Zhu et.al [6, 9] to be CF₄ and C₂F₆ as shown in formula (3) and (4).



After pre-electrolysis purification, the oxidation current begins to decrease at 4.2 V (vs. Li/Li⁺) resulting in anode effect. However, the drop in current is much more gradual than that before pre-electrolysis, and it does not drop to the minimum value until 4.9 V (vs. Li/Li⁺). Therefore, it can be inferred that oxygen ions concentration in molten salts has certain influence on the anode effect. In the reverse scanning process, as shown in Fig.1 (b), the curve after pre-electrolysis is basically the same as that of forward scanning, and the current peaks at the potential of 4.2 V (vs. Li/Li⁺). It can be concluded that 4.2 V (vs. Li/Li⁺) is a critical potential that generates anode effect. In another words, 4.2 V (vs. Li/Li⁺) should be the potential, at which the oxidation of fluorine ions and the production of perfluorocarbon occurs [9].

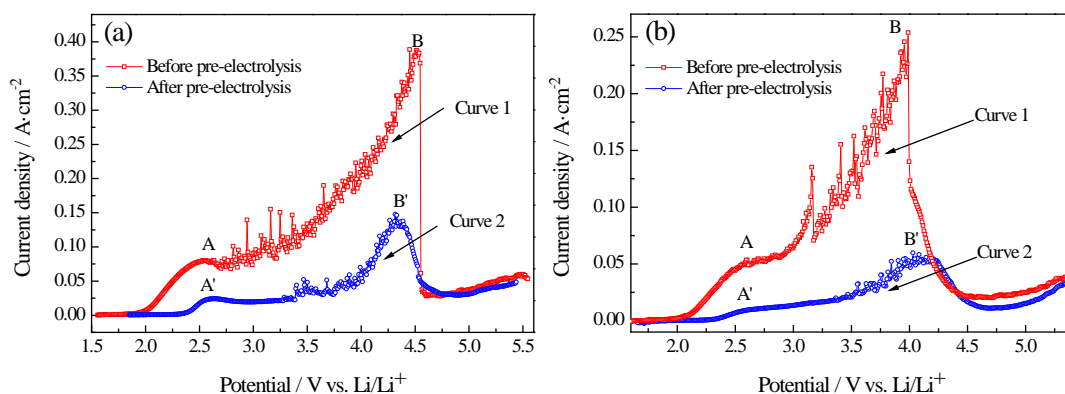


Fig.1. The cyclic voltammograms recorded on a graphite electrode in LiF-NdF₃ melt with scan rate of 100 mV/s at 1000°C. (a) Forward scan before (curve 1) and after (curve 2) pre-electrolysis, (b) Reverse scan before (curve 1) and after (curve 2) pre-electrolysis.

Fig.2 (a) shows the forward scanning part of the CVs recorded on a graphite electrode with different scan rates in the 5 hours pre-electrolyzed LiF-NdF₃ melt at 1000°C. With the increase of scan rate, the current density of the oxidation peak at 2.5 V (vs. Li/Li⁺) increased, and the peak potential slightly moves to a more positive position. In the range of 4.0 V-4.4 V (vs. Li/Li⁺), as the scan rate increases from 10 millivolts per second (mV/s) to 50 mV/s, the density of the oxidation current increases from 0.11 A/cm² to 0.15 A/cm², while the current remains basically unchanged at high scan rates from 50 mV/s to 200 mV/s. As shown in Fig.2 (b), the straight line derived from the current density of peak A vs the square root of scan rate in Fig.2 (a) goes through the origin. The result indicates that the adsorption of the oxidation products of oxygen ions is controlled by diffusion-controlled step, while the control process of CO/CO₂ gas evolution is electrochemical reaction step.

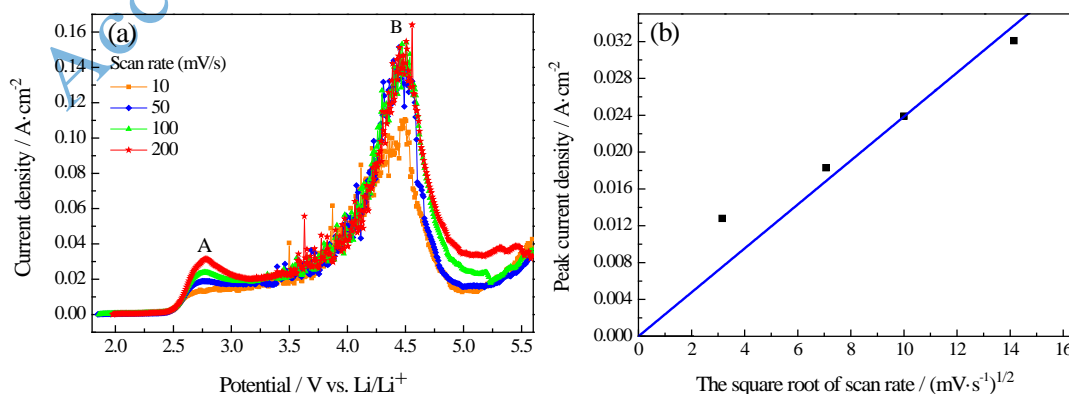


Fig. 2. (a) The forward scanning cyclic voltammograms recorded on a graphite electrode in the pre-electrolyzed LiF-NdF₃ melt with different scan rates at 1000°C. (b) Current density of peak A vs the square root of scan rate derived from (a).

In comparison with the forward scanning part of the CVs in Fig.2 (a), the current peak at 2.5 V (vs. Li/Li⁺) still appears during the reverse scanning process, but the peak current density of A' does not change at different scan rates, as shown in Fig.3 (a). In the range of 3.7 V-4.5 V (vs. Li/Li⁺), with the increase of scan rate, the peak current density in the reverse scanning process gradually decreases, and a new peak C' appears. Meanwhile, with the increase of scan rate, the peak potential of the newly occurred current peak C' moves to a more negative value, while the potential of the peak B' near 4.2 V (vs. Li/Li⁺) remains basically unchanged. Based on the previous judgement, it is believed that the peak at 4.2 V (vs. Li/Li⁺) is caused by fluorine ions oxidation. The new peak C' corresponds to the second step in the oxidation processes of oxygen ions.

The oxidation peak current density of B' shifts to a more negative value with the increasing scan rates from 10 mV/s to 300 mV/s. According to the studies in other molten salt systems, when anode effect occurs, the generation of PFCs will form a 'CF' insulating film on the surface of the graphite electrode, blocking the electrode reaction and leading to a sharp decrease in the current. In the process of forward scanning, due to the differences in electrode area and temperature, the critical potential required by the generated PFCs to completely cover the electrode surface and lead to the generation of anode effect will be different [11]. During reverse scanning, the desorption of PFCs on the surface of the graphite electrode is only controlled by potential, while the PFCs leaving the electrode is diffusion-controlled. This leads to obvious oxidation peaks at 4.2 V (vs. Li/Li⁺) with different scan rates during reverse scanning, which is caused by the fluoride ions oxidation and formation of PFCs. Thus, we can also prove that the generation of PFCs is strictly controlled by

the potential, and 4.2 V (vs. Li/Li⁺) is the critical potential to generate PFCs in LiF-NdF₃ melt at 1000°C.

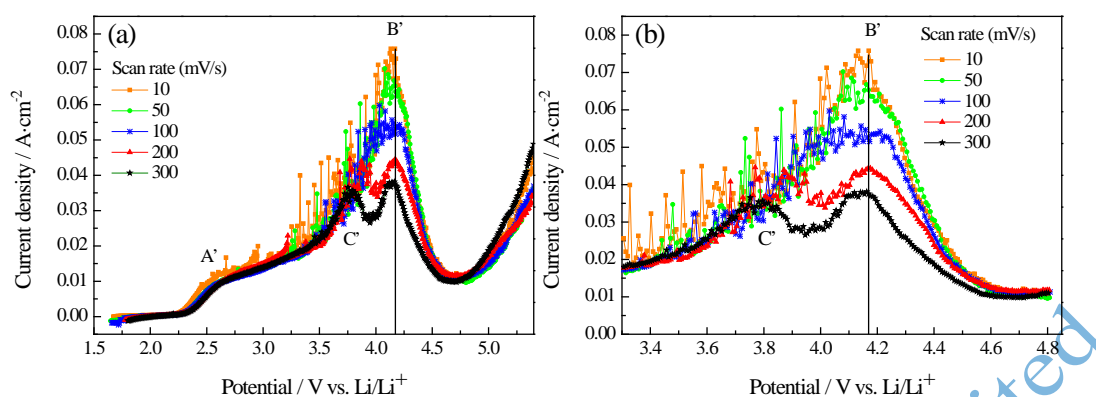


Fig. 3. (a) The reverse scanning cyclic voltammograms recorded on a graphite electrode in the pre-electrolyzed LiF-NdF₃ melt with different scan rates at 1000°C. (b) Larger and clarity part of (a) from 3.3 V-4.8 V (vs. Li/Li⁺).

3.2 Square wave voltammetry

The square wave voltammetry can provide a clearer redox process than the cyclic voltammetry. The conclusions obtained from the square wave voltammetry correspond to and verify those obtained from the cyclic voltammetry. The square wave voltammogram in Fig.4 (a) is recorded on a graphite electrode in the pre-electrolyzed LiF-NdF₃ melt with frequency of 25 hertz (Hz) at 1000°C. We can see clearly in the figure that there is a peak at 2.7 V (vs. Li/Li⁺) corresponding to the cyclic voltammograms in Fig.1 (a), which is caused by the oxidation of oxygen ions. The half-peak width ($W_{1/2}$) obtained by gaussian fitting on the oxidation peak at 2.7 V (vs. Li/Li⁺) in Fig.4 (b) is substituted into the following formula (5) for calculating the number of exchanged electrons [16]:

$$W_{1/2} = 3.52 \frac{RT}{nF} \quad (5)$$

R: universal gas constant; T: absolute temperature in K; n: number of exchanged electrons; F: Faraday's constant.

The number of exchanged electrons are calculated to be 1.63, verifying the

oxidation peak is a two-electron transfer oxidation process of oxygen ions. Subsequently, due to the release of gas, the square wave voltammogram also fluctuates violently. This is consistent with the previous conclusion that the oxygen ions oxidation is divided into two stages. Although the curve fluctuates wildly, the sharply drop of the current at 4.2 V (vs. Li/Li⁺) is clearly founded, and it reaches a minimum value around 4.6 V (vs. Li/Li⁺) before rising. This phenomenon once again indicates that 4.2 V (vs. Li/Li⁺) is a critical potential for the generation of anode effect in LiF-NdF₃ melt with lower oxygen content at 1000°C.

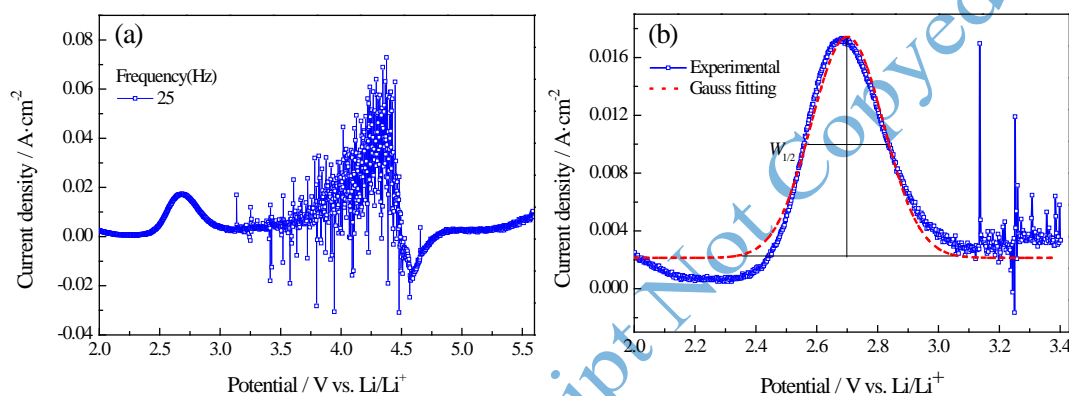


Fig. 4. (a) The square wave voltammogram recorded on a graphite electrode in the pre-electrolyzed LiF-NdF₃ melt with frequency of 25 Hz at 1000°C. (b) The Gauss fitting of the oxidation peak at 2.7V (vs. Li/Li⁺) in (a).

After 5 h pre-electrolysis of LiF-NdF₃ melt at 1000°C, the square wave voltammograms at different frequencies are superimposed to obtain Fig.5 (a). With the increase of frequency, the peak current at 2.7 V (vs. Li/Li⁺) also increases, while the square wave voltammograms in the later potential range from 3.0V-5.5V (vs. Li/Li⁺) remains coincident. The relationship between peak current of oxygen ions oxidation and square root of frequency in Fig.5 (b) derives from 2.3 V-3.1 V (vs. Li/Li⁺) in Fig.5 (a). This straight line, which is through the origin, is consistent with the results obtained from cyclic voltammetry. We may infer that the adsorption of oxygen ion oxidation products is controlled by diffusion-controlled step, while the control process of CO/CO₂ gas evolution is electrochemical reaction step.

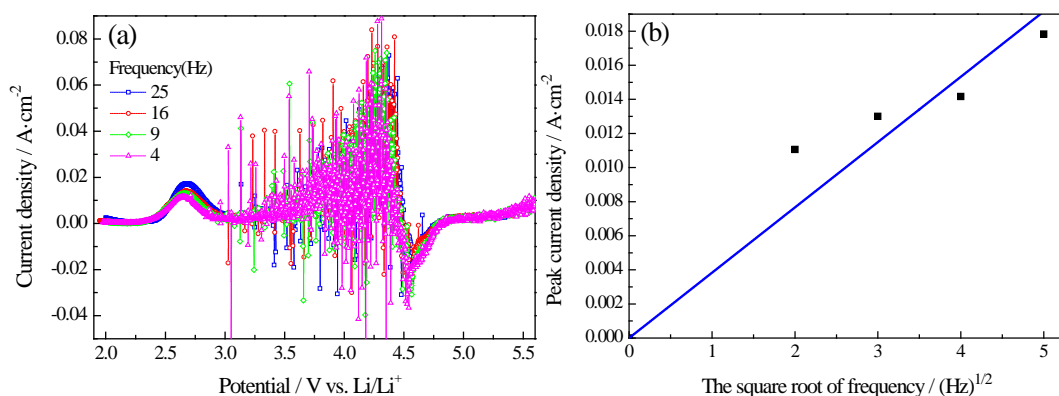


Fig. 5. (a) The square wave voltammograms recorded on a graphite electrode in the pre-electrolyzed LiF-NdF₃ melt with different frequency at 1000°C. (b) Peak current of oxygen ions oxidation vs the square root of frequency derived from 2.3 V-3.1 V (vs. Li/Li⁺) in (a).

3.3 Special situation after long time pre-electrolysis

During the experiment, we observed an interesting phenomenon that the cyclic voltammograms obtained in LiF-NdF₃ melt after long time pre-electrolysis (oxygen content: <150 ppm) sometimes appear as shown in Fig.6. The Fig.6 (a) and (b) respectively correspond to the curves obtained at scan rates of 100 mV/s and 300 mV/s. In these two figures, two peaks appear in the adsorption step of oxygen ions oxidation during the forward scanning process, while one peak remains during the reverse scanning process. The reason may be that different complexes are formed in molten salts, and the discharge of oxygen ion is turned into two-step electron transfer affected by the formation of complexes, corresponds to the two peaks in cyclic voltammograms.

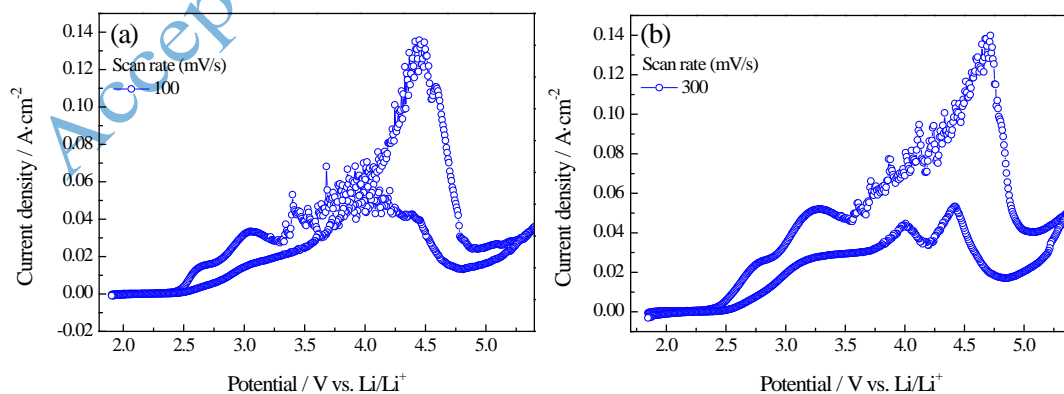


Fig. 6. The cyclic voltammograms recorded on a graphite electrode in the pre-electrolyzed LiF-NdF₃ melt at 1000°C. (a) Scan rate of 100 mV/s, (b) Scan rate of 300 mV/s.

In this case, the discrepancy between the measured square wave voltammograms in Fig.7 (a) and Fig.4 (a) is obvious. As is shown in Fig.7 (a), in the range of 2.4 V-3.4 V (vs. Li/Li⁺), two peaks also appear in the same position in comparison with Fig.6 (a). According to the calculation, the number of exchanged electrons in the redox reaction corresponding to the two peaks is 1.34 and 1.08, respectively, confirming the conclusion that the discharge process of oxygen ion is transformed into two-step electron transfer, one electron at each step.

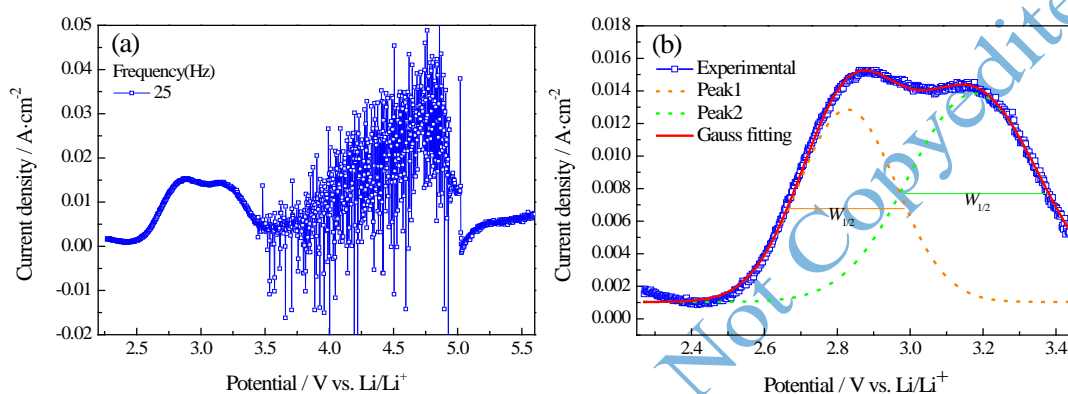


Fig. 7. (a) The square wave voltammogram recorded on a graphite electrode in the pre-electrolyzed LiF-NdF₃ melt with frequency of 25 Hz at 1000°C. (b) The Gauss fitting of the two peaks between 2.4 V-3.4 V (vs. Li/Li⁺) in (a).

4 Conclusions

In this paper, cyclic voltammetry and square wave voltammetry are used to explore the anode processes of LiF-NdF₃ melt after a long period of pre-electrolysis purification (oxygen content reduces from 413 ppm to 150 ppm).

- (1) The oxidation process of oxygen ions is divided into two stages, the oxidation products adsorption and CO/CO₂ gas evolution stage, respectively corresponding to the smooth and fluctuation current curve. The adsorption stage is controlled by diffusion-controlled step, while the control process of gas evolution is electrochemical reaction step.
- (2) After pre-electrolysis purification, when anode effect occurs, the decline amplitude of the current is much more gentle than that before pre-electrolysis, which indicates that oxygen ions in molten salts will have a certain impact on the anode effect.
- (3) The fluorine ions oxidation peaks at about 4.2 V (vs. Li/Li⁺) are clearly observed in the reverse scan processes, at which the oxidation of fluorine ions and the production of perfluorocarbon occur resulting in anode effect. It can be concluded that 4.2 V (vs. Li/Li⁺) is a critical potential that generates anode effect.
- (4) After a long time pre-electrolysis, it sometimes found that there are two oxygen ion oxidation peaks. According to the calculation, one electron transferred from each of the two peaks in the redox reaction. We speculate that the discharge process of oxygen ion is transformed into two-step electron transfer affected by the formation of complexes.

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