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Short communication

Electrochemistry of acetylide anion and anodic formation of carbon films in a LiCl–KCl–$CaCl_2$–CaC_2 melt

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ABSTRACT

The electrochemical deposition of carbon films on a nickel substrate was carried out through anodic oxidation of calcium acetylide dissolved in a LiCl–KCl–$CaCl_2$ melt at 823 K. Continuous and tenacious carbon films were prepared by a two-stage anodically potentiostatic deposition at a fast rate, and characterized by SEM, Raman spectroscopy, XRD and XPS. The results show the carbon films composed of micron-sized particles with graphitized and amorphous phases containing a mixture of sp^3 and sp^2 carbon. The cyclic voltammetry behavior of acetylide anion on graphite and nickel electrodes indicated that C_2^{2-} ions are oxidized more favorably on the nickel substrate due to the anodic depolarization from nickel carburization.

1. Introduction

There have been a lot of investigations of carbon films in the past twenty years due to their unique chemical and physical properties [1,2], which make them candidates for a number of technological applications [3–6]. They were mainly prepared by chemical or physical vapor deposition from gases. However, the vapor deposition methods are normally less cost-effective due to the rigorous reaction conditions and complex equipment. Furthermore, the growth rate of carbon films in the gases is very slow about microns per hour [7]. Other methods for deposition of carbon films from solutions at ambient pressure have been explored, as opposed to a low-density gas phase, indicating that faster deposition rates should be obtained [8]. Electrochemical deposition methods in the molten salts may be a promising way due to the moderate temperature and simplicity of the setup. Several reports on the preparation of carbon films by the cathodic electro-deposition in the molten salts containing some alkali carbonates have been published [9–13]. The metal acetylides in the ionic liquid (dimethyl sulfoxide) could also serve as carbon resource, and the diamond like carbon films with the high sp^3 content were obtained although the growth rate of such films was slow [8]. Carbon films deposited by the anodic oxidation of C_2^{2-} ions dissolved in the molten salts were documented only by Ito Y et al. [14]. They found that the carbon films were prone to exfoliate from the nickel substrate by folding the carbon film together with the substrate. In order to improve the adhesion of the carbon films, Li_3N was added into the electrolyte in Ito's patent [14]. However, Li_3N is moisture-sensitive, and unstable in the air. Furthermore, the carbon films would contain some nitrogen when Li_3N was introduced to the electrolyte.

In this communication, we prepared the carbon films on the nickel substrate by anodic deposition at a fast rate in LiCl–KCl–$CaCl_2$–CaC_2 melt without any Li_3N. Meanwhile, the nickel–C solid solution located between the carbon film and nickel substrate could increase the adhesion of the carbon films. In order to control the deposition potential, the cyclic voltammetry behavior of acetylide anion on the graphite and nickel electrodes was investigated. Based on the electrochemical results that were obtained, a feasible and fast process for preparation of carbon films was proposed.

2. Experimental

All the electrochemical experiments were carried out in a three-electrode system driven by an Auto Lab PGSTAT 320 N potentiostat under an argon atmosphere. The reference electrode was a Ag/AgCl (1.0 mol%) electrode, and the counter electrode was the aluminum spiral wire (Φ2 mm, 99.9% purity). Graphite rods (Φ6 mm, spectroscopically pure) and nickel wire (Φ2 mm, 99.9% purity) served as the working electrodes. The nickel wire was first polished with abrasive papers, and washed ultrasonically in anhydrous ethanol. The experimental setup was described in detail in our previous work [13]. Analytical grade LiCl–KCl–$CaCl_2$ (42:48:10 mol%) weighed about 420 g, previously dehydrated at 300 °C for 48 h, was used as the supporting electrolyte in

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an alumina crucible, and technical grade calcium acetylide as carbon source. Pre-electrolysis was performed under 2.8 V between two graphite rods before adding 1 mol% CaC_2 into the melt in order to remove redox active impurities. Potentiostatic electrodeposition of carbon films was conducted in two stages for 5 min in total at 823 K. Samples that were obtained were rinsed in de-ionized water to remove the residual salts and dried at room temperature. In order to obtain a distinct cross-section image of carbon films, some samples were coated with nickel films by electroless plating. The carbon films were characterized by XRD using a D/Max-2500PC (Rigaku, Japan), SEM by means of EVO18 (Carl Zeiss, Germany), Raman spectroscopy using Lab RAM HR800 (Jobin Yvon, France) and X-ray photoelectron spectroscopy with ESCALAB250 (Thermo, America).

3. Results and discussion

3.1. Cyclic voltammetry

The typical cyclic voltammogram with dash line in Fig. 1a shows the electrochemical window (EW) of the LiCl–KCl–$CaCl_2$ melt on a graphite electrode. The anodic limit, A_0 is the oxidation potential for chlorine evolution, which starting potential is defined as zero Volt, and all other redox couple potentials in this study are referred to this value. While the cathodic limit, R_1 is insertion of lithium and calcium ions into the graphite electrode, and its correspondingly anodic peak, A_1 is extraction of lithium-calcium from the electrode. When 1 mol% CaC_2 dissolves into the LiCl–KCl–$CaCl_2$ melt, the insertion of Li and Ca into the graphite occurs at −2.0 V, which is almost the same value as one in LiCl–KCl–$CaCl_2$, showing as cathodic wave $R_1^{'}$. The cathodic current R_2 becomes larger at −3.4 V due to deposition of Ca–Li alloys. The peak, A_1 of oxidation of Li and Ca changes to the shoulder of $A_1^{'}$, and the current wave of A_2 at −2.3 V should be the overlapped peaks due to extraction of Li and Ca from the graphite, and the irreversible oxidation of acetylide ions [15] shown in Eq. (1).

$$C_2^{2-} - 2e \rightarrow 2C \tag{1}$$

Other typical peaks on the anodic branch are likely due to the anodic behavior of oxygen ions on the graphite electrode, because technical grade calcium acetylide used here consists of about 85% CaC_2, and the rest, CaO, as the predominant impurity. Our assumption has been confirmed by the results shown in Fig. 1b, the cyclic voltammograms with various contents of CaO. Based on the relationship between the concentration of CaO and the height of the peaks that appeared on the anodic branches at the range from −1.75 to 0 V, this group of peaks is certainly due to the oxidation process of oxygen ions on the graphite electrode. The reactions are described as Eqs. (2)–(4) [16].

$$\text{PeakA}_3^{'} \text{ and PeakA}_3^{''}: xC + O^{2-} = C_xO(\text{adsorption}) + 2e \tag{2}$$

$$C_xO(\text{adsorption}) = CO + (x-1)C \tag{3}$$

$$\text{PeakA}_4: O^{2-} + C_xO - 2e \rightarrow CO_2 + (x-1)C \tag{4}$$

When the applied potential is more positive enough, the oxidation reaction (2)–(4) can occur, and the carbon deposited previously will be gasified.

Fig. 2 presents cyclic voltammograms on the nickel electrode in the KCl–LiCl–$CaCl_2$ melt with various additions of CaC_2. Because of alloying Ca and Li, the Ca–Li alloy deposition on the nickel in the melt occurs near −3.0 V, and becomes more rapid at −3.5 V, on which elemental Li and Ca can deposit separately and make the increase of cathodic current R_3 shown Fig. 2a. Reversing the potential scan then yields the anodic waves for the stripping of Li, Ca and their alloys, corresponding to the peak of A_6, and shoulders of A_7 and A_8, respectively. The anodic current limit of A_5 arising at −0.8 V is attributed to anodic dissolution of nickel into the chloride melt, and cathodic current wave R_5 is due to its reduction. Fig. 2b–d present the cyclic voltammograms in KCl–LiCl–$CaCl_2$ with various contents of CaC_2. During anodic scanning, there is the peak of A_9 arising for anodic deposition of carbon at −2.8 V, which is more negative than that of carbon deposit on the graphite electrode. In the case of the nickel electrode where dissolution of the deposited carbon can occur, it can yield a nickel–C solid solution [17], which introduces depolarization for the anodic deposition of carbon. With increasing of CaC_2 concentration in the melt, the height of the typical peak for carbon deposit increases, broadens and shifts to more positive potential. The broadening plateau, A_9 shown in Fig. 2d should be assigned to the convolution of the peaks for carburizing and depositing of carbon on the nickel electrode. The anodic peak of A_{10} at −1.3 V is attributed to the formation of nickel oxide films, and oxygen ions are introduced by technical grade calcium acetylide.

3.2. Potentiostatic deposition of carbon films on the nickel substrate

In order to prepare the carbon films on the nickel substrate, the potential applied should be more negative than that of oxidation of oxygen ions when the technical calcium acetylide serves as carbon source. Furthermore, the C–nickel solid solution should be formed before formation of carbon films in order to improve the adhesion of the carbon films to the nickel substrate. Based on the cyclic voltammetry results

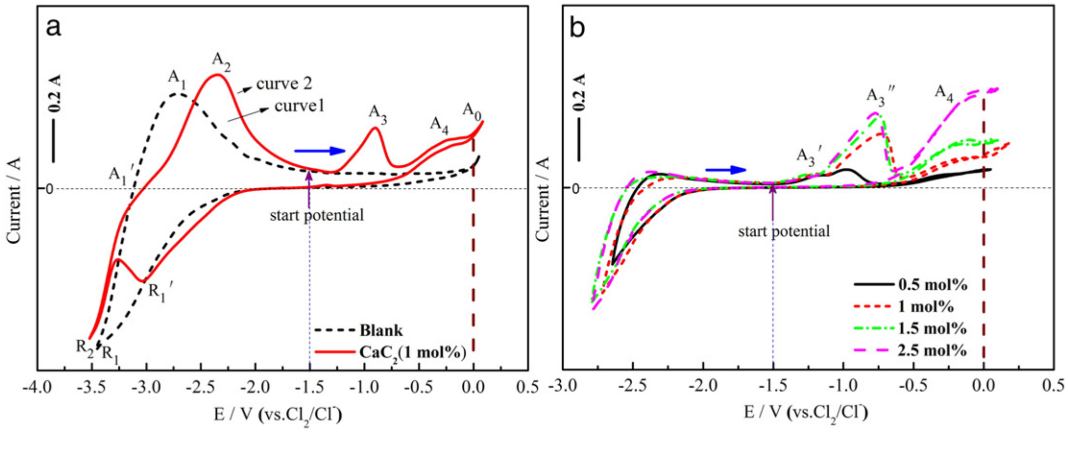

Fig. 1. CVs for a graphite electrode in (a) KCl–LiCl–$CaCl_2$ (dash line) and KCl–LiCl–$CaCl_2$–1 mol% CaC_2 (solid line) (b) CVs in the KCl–LiCl–$CaCl_2$ melt with different amounts of CaO (0.5, 1, 1.5, 2.5 mol%) at 823 K, scanning rate: 50 mVs^{-1}.