Electrochemical Behavior of Carbonate Ion in the LiF–NaF–Li₂CO₃ System

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ABSTRACT

The electrochemical behavior of carbonate ion at a Ni electrode in LiF–NaF–Li₂CO₃ molten salt was investigated using cyclic voltammetry, square wave voltammetry, and chronopotentiometry. The results show that the electrochemical reduction of carbonate ion at a Ni wire working electrode is a simple four-electron transfer that occurs in a one-step process. The reduction of carbonate ion at a Ni-wire working electrode is an irreversible process with diffusion-controlled mass transfer. The diffusion coefficient of carbonate ion at 973, 993, 1023, 1043, and 1063 K is 4.46 × 10⁻⁵, 4.82 × 10⁻⁵, 5.31 × 10⁻⁵, 5.90 × 10⁻⁵, and 6.54 × 10⁻⁵ cm²·s⁻¹, respectively, and the results obey the Arrhenius law, with an activation energy of 35.8 kJ mol⁻¹. The X-ray diffraction results show that hexagonally structured graphitized carbon can be obtained by potentiostatic electrolysis. Scanning electron microscopy images show that the deposits exhibit a spherical morphology.

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1. Introduction

The combustion of fossil fuels is regarded as the most significant source of the greenhouse gas carbon dioxide (CO₂). As economies develop, increasing amounts of carbon dioxide is being discharged into the atmosphere, which damages the ecological and environmental system and causes sea level rise. Meanwhile, CO₂ is an abundant and inexpensive carbon resource in the chemical industry. In recent years, increasing attention has been focused on converting CO₂ into useful chemicals such as HCOOH, CH₃OH, CH₄, CO, and C₇, using chemical transformation and electrochemistry methods. The recycling of CO₂ can reduce fossil fuel consumption on a large scale and CO₂ emissions can be consequently reduced. More recently, the conversion of CO₂ into high-value-added carbon and oxygen via electrolysis using solar energy to provide power has been considered one of the top research priorities all over the world. Some researchers have investigated the conversion of CO₂ into carbon or carbon monoxide by electrolysis in a molten salt. Carbon deposition has typically been achieved through the formation of carbon powders or carbon films. Carbon powder was produced in molten Li-I- Na–K carbonates under a CO₂ atmosphere at approximately 873 K. Kawamura et al. have developed a process based on the electrodeposition of carbon films on aluminum in fused LiCl–KCl–K₂CO₃ at 773 K. Massot et al. have obtained carbon films by electroreduction of Na₂CO₃ dissolved in molten LiF–NaF in the temperature range 973–1023 K. The mechanism of the conversion of carbon dioxide to carbon can be divided into two steps. First, carbon dioxide combines with oxygen ions in the molten salt, forming carbonate ions, as shown in Eq. (1):

\[ \text{CO}_2 + \text{O}^{2-} = \text{CO}_3^{2-} \quad (1) \]

Second, the carbonate ions are reduced to carbon at the cathode and produce oxygen at the anode in cases where an inert anode is used. However, two different views of the electrochemical reduction mechanism of the carbonate ion have emerged. Some authors have proposed that the reduction of carbonate ion to carbon occurs in a single step:

\[ \text{CO}_3^{2-} + 4e^- \rightarrow \text{C} + 3\text{O}^{2-} \quad (2) \]

However, a two-step process involving a hypothetical intermediate subcarbonate (CO₂⁻) that is further reduced to carbon and oxide ions has also been proposed:

\[ \text{CO}_3^{2-} + 2e^- \rightarrow \text{CO}_2^{2-} + \text{O}^{2-} \quad (3) \]

\[ \text{CO}_2^{2-} + 2e^- \rightarrow \text{C} + 2\text{O}^{2-} \quad (4) \]

Therefore, fundamental studies of the reduction mechanism for carbonate ion are still necessary. In this study, the electrochemical reduction mechanism of carbonate ions on a Ni working electrode was investigated using cyclic voltammetry, square wave voltammetry, and chronopotentiometry methods. LiF–NaF eutectic molten salt was chosen as the solvent for carbon dioxide electrolysis because it has high chemical stability and a low eutectic point. The standard potentials for the decomposition of alkali metal carbonate (Li₂CO₃, K₂CO₃, and Na₂CO₃) into carbon and alkali metal oxide were calculated, and the results clearly show that the electrochemical reduction of lithium carbonate into lithium oxide and carbon is highly favorable. Therefore, the LiF–NaF–Li₂CO₃ molten salt was chosen to investigate the reduction mechanism of carbonate ions.

2. Experimental

A schematic of the cell is shown in Fig. 1. The cell was a high graphite crucible placed in a cylindrical refractory steel vessel; it was capped with a stainless steel lid cooled by circulating water. The cell was heated using a programmable furnace, and the temperature was measured using a chromel-alumel thermocouple with an accuracy of ±1 K. A LiF–NaF eutectic mixture (molar ratio 61/39, analytical grade) was dried under vacuum for more than 72 h at 473 K to remove...
residual water. Pre-electrolysis was performed to remove residual water and some metal impurities. Carbonate ions were introduced into the bath in the form of lithium carbonate (Li₂CO₃, analytical grade) pellets. All of the experiments were performed under a dehydrated carbon dioxide atmosphere.

All of the electrochemical studies were performed using an AUTOLAB PGSTAT30 electrochemical workstation, and the measurements were controlled using the GPES software package. Cyclic voltammetry, square wave voltammetry and chronopotentiometry techniques were employed to investigate the electrochemical reduction mechanism of carbonate ions. The electrochemical experiments were performed using a three-electrode configuration. A Pt wire was used as the reference electrode, and the working electrode was nickel wire (ϕ 0.7 mm). The working electrodes were polished thoroughly with SiC paper and a polishing cloth, washed with alcohol, and then cleaned in distilled water by ultrasonication. The active electrode surface was determined by measuring the immersion depth of the electrode in the molten salt after each experiment. A graphite rod (ϕ 3.0 mm) was used as a counter electrode.

The morphology of the deposits was observed by scanning electron microscopy (SEM, SUPERSCAN SSX-550, acceleration voltage 15 kV) on an instrument equipped with an energy-dispersive X-ray spectrometer. The crystal structure and phase purity of the deposits were analyzed by X-ray diffraction (XRD, X’pert Pro, PANalytical Co.) using CuKα radiation; the samples were scanned over the 2θ range of 10° to 90° at a step of 5° min⁻¹.

3. Results and Discussions

3.1 Cyclic and squarewave voltammetry

To investigate the cathode electrode reaction in the electrochemical reduction of carbonate ions, we performed electrochemical studies using the cyclic voltammetry technique. The cyclic voltammetry experiments for the LiF–NaF and LiF–NaF–Li₂CO₃ melts were conducted using a Ni-wire working electrode; the results are shown in Fig. 2. A typical voltammogram obtained at 1023 K in the blank LiF–NaF melt is represented by the dotted line in Fig. 2. This result shows that huge cathode current begins at approximately −1.5 V vs. Pt; the cathodic limit corresponds to alkali-metal deposition. When Li₂CO₃ was added to the molten LiF–NaF, the cyclic voltammogram showed that an additional reduction current peak at approximately −1.4 V vs. Pt, as shown in Fig. 2. During the reverse scan, the oxidation peak observed at approximately −1.4 V vs. Pt was related to the oxidation of the alkali metal. However, no additional anodic peak was observed, which suggests the cathode process is irreversible.

Square wave voltammetry has been carried out to calculate the number of electrons involved in the carbonate ion reduction process. The square wave voltammograms obtained at the Ni working electrode in the LiF–NaF–Li₂CO₃ molten salts is presented in Fig. 3. The reduction-peak potentials observed in the square wave voltammogram is the same with that observed in the cyclic voltammogram. The W₁/₂ of the square wave voltammogram depends on the number of transferred electrons and temperature by the following relation:

\[ W_{1/2} = 3.52 \frac{RT}{nF}, \]  

Where \( W_{1/2} \) is the half peak width (V), \( R \) is the gas constant (8.314 J mol⁻¹ K⁻¹), \( T \) is the temperature (K), \( F \) is the Faraday constant (96,485 C mol⁻¹), \( n \) is the number of exchanged electrons. The value of \( n \) calculated at frequency of 10 Hz is 3.89, close to four.
electrons. On the basis of the cyclic voltammetry and square wave voltammetry analysis results, potentiostatic electrowinning experiments were performed at potentials between −1.5 and −0.6 V vs. Pt. There is no faradic current till −0.9 V. However, black deposits were observed on the Ni electrode when the electrode was used for electrowinning at potentials between −1.5 and −0.9 V. The deposits were analyzed by XRD; the results indicate that the deposits are carbon, as shown in section 3.4. At these potentials, only the electrochemical reduction of carbonate ion to carbon occurs. None of the electrolytes led to CO$_2$ generation. The results demonstrate that the reduction process of carbonate ion can be written as CO$_3^{2−}$ + 4e$^{-}$ → C + 3O$^2−$; i.e., the reduction of carbonate ion is a one-step process.

We performed a series of cyclic voltammogram experiments in more detail to study the deposition kinetics and to determine the diffusion coefficient of carbonate ion in LiF–NaF–Li$_2$CO$_3$ molten salts. The voltammograms obtained with a Ni wire working electrode at scan rates ranging from 0.05 V s$^{-1}$ to 0.20 V s$^{-1}$ are shown in Fig. 4. As evident in Fig. 4, the cathodic peak potential shifted negatively with increasing scan rate. In addition, no corresponding anodic peaks were observed in the reverse scan. These results further confirmed that the reduction of carbonate ion is an irreversible process.

For an irreversible electrochemical reaction process, the relationship between $ω$ and $|E_p−E_{p/2}|$ is shown in Eq. (6).$^{28,29}$

$$|E_p − E_{p/2}| = \frac{1.857RT}{anF}.$$

(6)

where $E_p$ is the peak potential, $E_{p/2}$ is the half-peak potential, $R$ is the gas constant, $T$ is the temperature (K), $F$ is the Faraday constant, $n$ is the number of exchanged electrons ($n = 4$), and $α$ is the charge-transfer coefficient. On the basis of the $E_p$ and $E_{p/2}$ values extracted from the CV curve obtained at a potential scan rate of 0.07 V s$^{-1}$, the value of $α$ calculated using Eq. (6) was 0.21.

Figure 5 highlights the directly proportional relationship between the cathodic peak current ($i_p$) and the square root of the potential scan rate ($ν^{1/2}$). A linear relationship between $i_p$ and $ν^{1/2}$ is clearly evident, which indicates that the reduction of carbonate ion on a Ni wire working electrode is a diffusion-controlled process.$^{30}$ Thus, we concluded from the cyclic voltammogram study that the reduction of carbonate ion on a Ni electrode in LiF–NaF–Li$_2$CO$_3$ molten salt is an irreversible and diffusion-controlled process.

Because carbonate ion reduction on a Ni electrode in LiF–NaF–Li$_2$CO$_3$ molten salt is a diffusion-controlled, irreversible electrochemical reaction, the diffusion coefficient ($D$) of carbonate ion in LiF–NaF–Li$_2$CO$_3$ can be calculated by the relationship between the cathodic peak current and the square root of the potential scan rate established by Delahay’s equation:$^{29}$

$$i_p = 0.4958 \left( \frac{anF}{RT} \right)^{1/2} nF(Dv)^{1/2} C_{CO_3^{-}}.$$

(7)

where $A$ is the electrode area (cm$^2$), $C_0$ is the carbonate-ion concentration (mol cm$^{-3}$), $D$ is the diffusion coefficient (cm$^2$ s$^{-1}$), $F$ is the Faraday constant, $n$ is the number of exchanged electrons ($n = 4$), $ν$ is the potential scan rate (V s$^{-1}$), $R$ is the gas constant, $T$ is the temperature, and $α$ is the charge-transfer coefficient. Combining Eqs. (6) and (7), we calculated the diffusion coefficient ($D$) for the reduction process of carbonate ion at 1023 K to be $5.31 \times 10^{-3}$ cm$^2$ s$^{-1}$. This value is smaller than that of $6.51 \times 10^{-3}$ cm$^2$ s$^{-1}$ reported by Massot et al., who reduced carbonate ion in LiF–NaF–Na$_2$CO$_3$ at 1023 K.$^{25}$ The difference between these values may result from the different concentrations of the carbonate ions and the different of alkali-metal carbonates used.

3.2 Chronopotentiometry study

To confirm that the electrochemical reduction of carbonate ion is controlled by a diffusion process, we performed chronopotentiometric experiments on a Ni electrode in LiF–NaF–Li$_2$CO$_3$ melts. Typical chronopotentiograms of carbonate ion obtained under various applied current intensities at 1023 K are shown in Fig. 6a. As evident in Fig. 6a, the chronopotentiograms exhibit two potential plateaus. The first potential plateau at approximately −1.4 V vs. Pt is associated with the reduction of carbonate ions to carbon, as previously observed in the cyclic voltammograms. After approximately 0.5 s, the electrode potential reaches a limiting value corresponding to the deposition of alkali metal. The potential of the first plateau in the chronopotentiometric curves shifted toward negative potentials with increasing current intensity, which confirms that the electrochemical reduction of carbonate to carbon is an irreversible process.$^{29}$ Moreover, the transition time ($τ$) decreases when the applied cathodic current increases. As shown in Fig. 6b, the current intensity ($I$) exhibits a good linear relationship with the transition time ($τ$), which verifies Sand’s law [Eq. (8)] and suggests that the electrochemical reduction of carbonate ions is a diffusion-controlled process:$^{29}$

$$i\sqrt{τ} = \frac{nFCA\sqrt{πD}}{2} = \text{constant},$$

(8)
constant, $n$ is the number of exchanged electrons ($n = 4$), $D_0$ is the diffusion coefficient, $k^0$ is the standard rate constant, and $\tau$ is the transition time.

The plots of $E$ vs. $\log(\tau^{1/2} - t^{1/2})$ at different applied current intensities are shown in Fig. 6c. Excellent linear relationships between $E$ and the value of $\log(\tau^{1/2} - t^{1/2})$ were obtained at different current intensities. These results further demonstrate that the reduction of carbonate ion is an irreversible process. The slope (2.303RT/OnF) obtained for curves recorded at several current intensities is very close to 0.16, and the value of $\alpha$ was calculated to be 0.32. This value of $\alpha$ is larger than that determined by cyclic voltammetry; this difference may be a consequence of the different electrochemical techniques used for the measurements.

### 3.3 Diffusion coefficient of carbonate ions and activation energy

The sensitivity of the diffusion rate to temperature is related to the diffusion activation energy. A higher diffusion activation energy means that the diffusion rate is more sensitive to a change in temperature. In contrast, a lower diffusion activation energy means that the diffusion rate is less sensitive to a change in temperature.

The influence of the temperature on the value of the diffusion coefficient was investigated using cyclic voltammetry. We performed a series of cyclic voltammograms on a Ni electrode in the scan range from $-1.6 \text{ V}$ to $-0.5 \text{ V}$ vs. Pt at different potential scan rates between 0.05 and 0.20 V s$^{-1}$ and at several different temperatures (i.e., 973, 993, 1023, 1043, and 1063 K). The values of the diffusion coefficient calculated at different temperatures are shown in Table 1.

According to Arrhenius’ law, a relationship exists between the diffusion coefficient and the activation energy, as shown in Eq. (10):21

$$D = D^0 \exp \left(-\frac{E_a}{RT}\right),$$

where $E_a$ is the activation energy (kJ mol$^{-1}$), $D$ is the diffusion coefficient (cm$^2$ s$^{-1}$), $D^0$ is the frequency factor, $R$ is the gas constant, and $T$ is the temperature.

As shown in Fig. 7, $\ln D$ and $1/T$ also exhibit a linear relationship:

$$\ln D = -\frac{5.6023 - \frac{4308.5}{T}}{T},$$

where $D$ is in cm$^2$ s$^{-1}$ and $T$ is in K.

From this relationship, we determined the $E_a$ to be 35.8 kJ mol$^{-1}$. This result shows that the effect of temperature on the diffusion coefficient is small. The obtained value of $E_a$ is higher than the value (21.2 kJ mol$^{-1}$) reported by Massot et al.23 This difference may be a consequence of the different alkali-metal carbonates used in the experiments.

### 3.4 Potentiostatic electrolysis analysis

To confirm the reduction mechanism of carbonate ion suggested by the cyclic voltammetry results, we performed potentiostatic
electrolysis experiments using a Ni electrode in the LiF–NaF–Li2CO3 melt at 1023 K. Black deposits were obtained on the Ni electrode after electrolysis for 6 h. The deposits were washed with dilute hydrochloric acid and deionized water to eliminate the coherence salt.

The structural features and the morphology of the deposits were characterized by XRD and SEM. The XRD patterns and SEM images of the deposits are shown in Fig. 8 and Fig. 9, respectively.

The XRD patterns of the deposits show a sharp peak at a 2º angle of 26.4º, which we indexed as the (002) peak of hexagonally structured graphitized carbon (Fig. 8). Other peaks at approximately 42.3º, 44.4º, 50.6º, 54.5º, 77.4º, and 83.6º correspond to the (100), (101), (102), (004), (110), and (112) reflections, respectively. However, according to the XRD standard card for graphite, the (103) reflection peak at 59.9º is missing. The crystallinity of the carbon is reflected by the interlayer distance (d002). The d002 value deduced by the Bragg method was 0.337 nm; this value is similar to the theoretical value obtained for pure graphite (0.335 nm). The sharp shape of the (002) diffraction line is evident in Fig. 8; the sharpness of this line indicates that the deposited carbon exhibits good crystallinity.

Figure 9a shows that the deposit has a spherical structure, which is clearly defined at a higher resolution (Fig. 9b). The energy-dispersive X-ray spectroscopy (EDS) analysis results indicate that the deposits are carbon; no other elements were detected, as shown in Fig. 9c.

4. Conclusions

The electrochemical reduction of carbonate ion on a nickel electrode in LiF–NaF–Li2CO3 melts was investigated. The results of the electrochemical techniques confirmed that the electrochemical reduction mechanism of carbonate ion in the LiF–NaF–Li2CO3 melts is a simple four-electron transfer in a one-step process. The cyclic voltammetry and chronopotentiometry results indicated that the reduction of carbonate ion was an irreversible process through diffusion-controlled mass transfer. The diffusion coefficient of carbonate ion was calculated by cyclic voltammetry and showed a temperature dependence according to Arrhenius’ law:
The deposits deposited during potentiostatic electrolysis at a potential of $-1.4$ V vs. Pt were characterized by XRD and SEM-EDS analysis. The results revealed that the deposits are hexagonally structured graphitized carbon. SEM images revealed that the deposits exhibited a spherical morphology. In this work, crystallized carbon was deposited onto nickel cathodes by potentiostatic electrolysis. The form of carbon deposited appears to be related to the cathode material.

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