Electrochemical Formation of Thin Carbon Film from Molten Chloride System

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ABSTRACT

Cathodic reduction of carbonate ion in LiCl-KCl eutectic melt was investigated at 400-500°C (mainly at 450°C) using cyclic voltammetry and chronopotentiometry. In the voltammogram, two cathodic peaks were observed at 0.8V and 0.5V (vs. Li/Li⁺), respectively. The former was ascribed to the reduction of carbonate ion to form elementary carbon and the latter was ascribed to the intercalation of reduced lithium into the electrodeposited carbon layer. On the other hand, three anodic peaks were observed. The peak observed at the most negative potential was ascribed to the anodic dissolution of intercalated lithium and the other two, at 1.8V and 2.1V (vs. Li/Li⁺) respectively, were concluded to be due to the irreversible anodic oxidation of carbon, through a series of the slow back reactions of

(a) \( \text{CO}_3^{2-} + 2e^- = \text{CO}_2 + \text{O}_2^- \)

and

(b) \( \text{CO}_2^{2-} + 2e^- = \text{C} + 2\text{O}^- \).

Diffusion coefficient of carbonate ion was estimated to be \( 1.66(\pm 0.05) \times 10^{-5} \text{ cm}^2\text{s}^{-1} \) at 450°C, and the activation energy of diffusion was estimated to be \( 1.43(\pm 0.15) \text{ kJ mol}^{-1} \).

By potentiostatic and galvanostatic macroelectrolysis, various types of film were obtained at the cathode depending on the electrolytic conditions. From the analysis by RBS, ESCA, X-ray diffraction and Raman spectroscopy, these films were concluded to be amorphous carbon.

INTRODUCTION

The electrochemical formation of carbon film from molten halide is an interesting research subject since this can be considered as one of the candidate electrochemical \( \text{CO}_2 \) fixation processes to obtain valuable product. The \( \text{CO}_2 \) fixation can be achieved through the following two steps: First, \( \text{CO}_2 \) gas is supplied into molten halide containing oxide ion, to form carbonate ion. And then, by the electrolysis, cathodic reduction of carbonate ion takes place to form various types of carbon film on the cathode, depending on the electrolytic conditions. This report describes the results of experiments conducted by using LiCl-KCl eutectic melt containing carbonate ion which exemplified the possibility of the latter step of the above process. The results obtained here also provide useful information for considering the electrodeposition of metal carbides from halide melts containing the mixture of oxyanion of the metal and \( \text{CO}_3^{2-} \) ion.
**EXPERIMENTAL**

First of all, the electrochemical behaviour of carbonate ion at nickel cathode in LiCl-KCl eutectic melt was investigated at 400-550°C (mainly at 450°C) using cyclic voltammetry and chronopotentiometry, in order to realize that the aimed reaction can really occur, as well as to clarify the reaction mechanism. All chemicals were of reagent grade (Wako Chemicals Co., Ltd.) and were dried under vacuum for several days at 200°C. After melting the salt, argon gas was bubbled into the melt for several hours to remove contaminated water further. By this procedure, residual cathodic current density could be reduced to less than $2 \times 10^{-3}$ A cm$^{-2}$ at 1.3V (vs. Li/Li$^+$) at a scan rate of 0.1V s$^{-1}$. An Ag/Ag$^+$ electrode was used as the reference electrode, which comprises a silver wire and chloride (1 mol% AgCl) that were both contained in a pyrex glass tube which had a very fine tip. The potential of this reference electrode was calibrated against an alkali metal electrode, Li/Li$^+$, that was prepared by the electrodeposition of Li on a nickel wire [1]. Unless otherwise stated, all potentials are reported with respect to the potential of Li/Li$^+$ couple in the melt. Glassy carbon rod was used as an anode. After preparing the solvent melt, vacuum-dried potassium carbonate was added to a concentration of 0.02 - 1.0%.

After a series of cyclic voltammetry and chronopotentiometry experiments, potentiostatic and galvanostatic macroelectrolysis were conducted using several kinds of cathode materials including nickel and aluminum. The electrolytic conditions were determined based on the voltammograms as well as the chronopotentiograms obtained in the above experiments. The electrodeposited samples were taken out of the cell, washed with distilled water, dried and kept in a desiccator. The samples were then subjected to analysis using SEM, EPMA, EDX, ESCA, RBS, XRD and Raman spectroscopy.

**RESULTS AND DISCUSSION**

1. Reaction Mechanism

Typical cyclic voltammogram is shown in Fig.1[2]. Two cathodic peaks B and C are observed at 0.8V and 0.5V, respectively. And three anodic peaks, D, E and F are also observed.

1.1 Cathodic Reaction

Figure 2 shows relation between peak current density of Peak B and the concentration of added carbonate ion, and Figure 3 shows relation between peak current density of Peak B and potential scan rate. These linear relations suggest that the reaction is diffusion controlled. As for Peak C, it seems to appear due to the formation of intercalation compound between electrodeposited carbon and lithium [3]. Thus, cathodic peak concerning the reduction of carbonate ion is only Peak B. And as will be described later, electrodeposition of elementary carbon was confirmed by the analysis of the product obtained at...
the peak potential of B. Then, cathodic reduction of carbonate ion is simply expressed as:

\[
\text{CO}_3^{2-} + 4e^- = C + 30_2^- \quad (1).
\]

Figure 4 shows relation between the potential of Peak B and potential scan rate \(v\). The peak potential shifts to the negative direction linearly with \(\log v\) \([4]\). This indicates that the following theoretical relation for the irreversible reaction \([5]\) can be applied:

\[
\frac{dE_p}{d(\log v)} = -\frac{2.303RT}{n_a F} \quad (2),
\]

where \(n_a\) is the number of electrons involved in the rate determining elementary step. From the slope of the line in Fig.4, \(n_a\) for Peak B is estimated to be \(1.04(\pm 0.20)\). The \(n_a\) value can also be estimated from the peak width. This was determined to be \(0.89 (\pm 0.13)\), according to the following equation \([5]\):

\[
E_p - E_{p/2} = -1.859 \frac{RT}{n_a F} \quad (3).
\]

These two values are in fairly good agreement.

1.2 Anodic Reaction

Let us then consider Peak E which appears at the anodic scan, applying the theoretical relation:

\[
E_{pa} - E_{pa/2} = \Gamma \frac{RT}{(n - n_a) F} \quad (4),
\]

Here, \(n\) is the number of electrons involved in the total reaction, and \(n_a\) is the number of electrons involved in the rate determining elementary step.

This relation is derived for the case of anodic reaction of the product formed at the electrode surface by the cathodic reduction of complex ion with coordination number \(m\). \(\Gamma\) in eqn(4) is a constant which is given as:

\[
\Gamma = 1.839, 2.588, 3.288 \quad (m = 1, 2, 3)
\]

depending on the coordination number \(m\) \([5]\). From the width of Peak E, \(0.13 (\pm 0.07)\), \((n - n_a)\) is calculated to be:

\[
n - n_a = 0.88 (\pm 0.05), 1.24 (\pm 0.07), \quad \text{and} \quad 1.58 (\pm 0.09)
\]

for the \(m\) value of 1, 2 and 3, respectively. Accordingly, \(n\) is calculated to be 1.77, 2.13 and 2.47 for \(m = 1, 2\) and 3, respectively. These values are all around 2, which is very different from the value 4 for the number of electrons for reaction (1). This can be understood if we assume that the reaction (1) proceeds through 2 electron reaction steps (5) and (6). That is, in Fig.1, carbonate ion in the solution is reduced to divalent carbon, which is immediately reduced to elementary carbon. But at Peak E which corresponds to the
reverse reaction of Peak B, reaction from divalent to tetravalent carbon does not proceed even when elementary carbon is reduced to divalent carbon, and divalent ion is considered to diffuse to the bulk solution. Chemical form of divalent carbon ion may be $CO_2^{2-}$, as proposed by Delimarskii et al [6]. Thus, Peak F is considered to be ascribed to the anodic oxidation of $CO_2^{2-}$ to form $CO_3^{2-}$ ion.

$$\text{CO}_3^{2-} + 2e \xrightarrow{\text{slow}} \text{CO}_2^{2-} + \text{O}^2- \quad (5)$$

$$\text{CO}_2^{2-} + 2e \xrightarrow{\text{fast}} \text{C} + 2\text{O}^2- \quad (6).$$

Concludingly, Peak B corresponds to the forward reaction of (5) + (6), Peak E corresponds to the back reaction of reaction (6), and Peak F corresponds to the back reaction of reaction (5).

As reactions (5) and (6) are both elementary processes and thus $n_a = n = 2$, peak potential difference can be written as:

$$E_p - E_p = \frac{2.53 \cdot RT}{nF} + \frac{RT}{\alpha(1-\alpha)nF} \{-(2.303+0.215\alpha)\log \Lambda - 5.69 + 6.17\alpha\} \times$$

$$\frac{RT}{\alpha(1-\alpha)nF} \quad (7).$$

From this equation, reversibility parameter $\Lambda$ defined by equation (9) can be obtained. And from equation (8) and the peak potential of Peak B, $E_o = 0.743V$, standard potential $E^*$ can be determined. Furthermore, standard rate constant $k^*$ can be also determined from the $\Lambda$ value, according to equation (9).

$$E_p - E^*_o = -1.16 \frac{RT}{nF} + 2.303(\log \Lambda + 2.475) \frac{RT}{\alpha nF} \quad (8)$$

$$k^* = \sqrt{\frac{nF}{RT}} \cdot \Lambda \quad (9).$$

Here, $E_o$ and $k_o$ are defined as:

$$E^* = \frac{RT}{nF} \ln \left(\frac{k_f}{k_b^*}\right) \quad (10)$$

and

$$k^* = k_f^{1-\alpha} k_b^{\alpha} \quad (11).$$

Reversibility factor $\Lambda$ are obtained as:

$$\log \Lambda^{(5)} = -5.53$$

and

$$\log \Lambda^{(5)} = -4.50$$

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respectively, since potential differences between Peak B and Peak C, and Peak B and Peak F are 1.07 and 1.38(V), respectively, at the scan rate of 0.4Vs⁻¹. Furthermore, E° 's are determined to be 1.27 and 1.11, respectively, and k° 's are determined to be 1.06×10⁻⁵ and 1.13×10⁻⁴(cm·s⁻¹), respectively.

Figure 5 shows the comparison between experimental and calculated voltammogram[4]. The calculation was conducted using the parameters obtained above. The fairly good agreement suggests that the above discussion is reasonable.

Figure 6 shows typical chronopotentiogram. Only one plateau can be observed here, which also shows the appropriateness of the above conclusion that the cathodic reaction (1) proceeds by single step or by a consecutive step involving slow reaction (5) immediately followed by fast reaction (6).

2. Diffusion Coefficient of Carbonate Ion

From the experimental data of cyclic voltammetry shown in Figs. 2 and 3, diffusion coefficient of carbonate ion D₀ is estimated to be:

$$D₀ = 1.6 (±0.4) \times 10⁻⁵ \text{ (cm}² \text{ s}⁻¹)$$

with the use of equation (12):

$$i₀ = -0.455nFAC₀\sqrt{\frac{\alpha naF}{RT}D₀}$$

(12).

Figure 7 shows relation between transition time τ and $C₀/i²$ obtained by chronopotentiometry. As equation:

$$\sqrt{\tau} = \frac{\sqrt{πD₀nFAC₀}}{2i}$$

(13) holds for both reversible and irreversible reaction, diffusion coefficient of carbonate ion is thus estimated to be:

$$D₀ = 1.66 (±0.05) \times 10⁻⁵ \text{ (cm}² \text{ s}⁻¹)$$

This value is coincident with the value obtained by cyclic voltammetry.

Figure 8 shows Arrhenius plot of diffusion coefficient. From this figure, activation energy of the diffusion is estimated to be:

$$ΔE_a = 1.43 (±0.15) \text{ (kJ mol}⁻¹)$$

3. Electrodeposition of Carbon Film

Figures 9 and 10 show SEM images of film potentiostatically electrodeposited on Ni substrate and Figures 11 and 12 show those potentiostatically electrodeposited on Al substrate [7].

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Figure 13 and Figure 14 show those galvanostatically electrodeposited on Al substrate. Various morphologies are obtained depending on the potential. Especially, it is interesting to see fiber like carbon in Figs. 10 and 15. Figures 16, 17, 18 and 19 show an example of RBS spectrum, ESCA spectrum, XRD pattern and Raman spectrum of film, respectively. These data show that the electrodeposited films are amorphous carbon.

CONCLUSION

Cathodic reduction of carbonate ion in LiCl-KCl eutectic melt was investigated at 400-550°C (mainly at 450°C) using cyclic voltammetry and chronopotentiometry. Cathodic reduction of carbonate ion to form elementary carbon is concluded to proceed by single step reaction:

\[ \text{CO}_3^{2-} + 4e = C + 3\text{O}_2^- \]

or by a consecutive reaction involving slow reaction:

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

immediately followed by:

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

On the other hand, anodic dissolution of carbon to form carbonate ion is concluded to proceed through a series of the slow back reactions of the latter two.

Diffusion coefficient of carbonate ion was estimated to be \(1.66(\pm 0.05) \times 10^{-5} \text{cm}^2 \cdot \text{s}^{-1}\) at 450°C, and the activation energy of diffusion was estimated to be \(1.43(\pm 0.15) \text{kJ} \cdot \text{mol}^{-1}\).

By potentiostatic and galvanostatic macroelectrolysis, various types of film were obtained depending on the electrolytic conditions. From the analysis by RBS, ESCA, XRD and Raman spectroscopy, these films were concluded to be amorphous carbon.

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Fig.1 Voltammogram
LiCl-KCl, 450°C, Ni electrode, [CO$_3^{2-}$] : 0.2mol%, Scan rate : 0.2V $\cdot$ s$^{-1}$

Fig.2 Relation between Current Density of peak B and [CO$_3^{2-}$]
LiCl-KCl, 450°C, Ni electrode, Scan rate V $\cdot$ s$^{-1}$
■:0.1, +:0.2, ♦:0.4, ▲:0.7, ×:1.0

Fig.3 Relation between Current Density of peak B and scan rate
LiCl-KCl, 450°C, Ni electrode, [CO$_3^{2-}$] (mol)%
■:0.1, +:0.2, ♦:0.4, ▲:0.7

Fig.4 Potential of peak B against $\log \sqrt{v}$
LiCl-KCl, 450°C, Ni electrode, [CO$_3^{2-}$] (mol)%
○:0.1, +:0.2, ×:0.4, ●:0.7
Fig. 5 Experimental and calculated voltamogram as the model:

(a) \( \text{CO}_3^{2-} + 2e \rightleftharpoons \text{CO} + 2\text{O}_2^{2-} \)  
(b) \( \text{CO} + 2e \rightleftharpoons \text{C} + \text{O}_2^{2-} \)

LiCl-KCl, 450°C, Ni electrode, \([\text{CO}_3^{2-}] = 0.2 \text{ mol} \cdot \text{L}^{-1}\). Scan rate: 0.4 V \cdot \text{s}^{-1}

---: Data from experiment,  
---: Calculated value for reaction (a)  
---: Calculated value for reaction (b),  
---: (a) + (b)

Fig. 6 Chronopotentiogram

LiCl-KCl, 450°C, Ni electrode,

---: \([\text{CO}_3^{2-}] = 0.1 \text{ mol} \cdot \text{L}^{-1}\)
---: blank data
A: Reduction of carbonate ion  
B: Reduction of lithium ion

Fig. 7 Relation between \( t \) and \( (\text{CO}/i)^2 \)

LiCl-KCl, 450°C, Ni electrode.
Fig. 8 Arrhenius plot of diffusion coefficient of $\text{CO}_3^{2-}$
LiCl-KCl, Ni electrode

Fig. 9 Surface SEM Image of Carbon Deposits on
Ni Substrate (0.5V vs. Li/Li$^+$)

Fig. 10 Surface SEM Image of Carbon Deposits on
Ni Substrate (1.0V vs. Li/Li$^+$)
Fig. 11  Surface SEM Image of Carbon Deposits on Al Substrate (0.9V vs. Li/Li⁺)

Fig. 12  Surface SEM Image of Carbon Deposits on Al Substrate (1.0V vs. Li/Li⁺)

Fig. 13  Surface SEM Image of Carbon Deposits on Al Substrate (1.0mA/cm²)
Fig. 14 Surface SEM Image of Carbon Deposits on Al Substrate (2.0mA/cm²)

Fig. 15 Surface SEM Image of Carbon Deposits on Al Substrate (2.0mA/cm²)

Fig. 16 RBS Spectrum of Film Electrodeposited at 0.6V
Fig. 17 ESCA Spectrum of Film Electrodeposited at 1.1V

Fig. 18 X-ray Diffraction Pattern (Co-Kα) of Film Electrodeposited at 0.4V