

# Formation of a dense carbon film by cathodic reduction of $\text{CO}_3^{2-}$ ions in a molten salt

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## Abstract

In order to meet the needs of the time to form a hard and smooth surface on various materials, novel carbon coating methods for applying a molten salt electrochemical process (MSEP) are currently being developed by the authors. This paper describes the interesting results obtained during a series of experiments on the formation of carbon film by the cathodic reduction of  $\text{CO}_3^{2-}$  ions in molten salt. The experiments were conducted under various different electrolysis conditions, such as concentration of  $\text{CO}_3^{2-}$  ions, temperature of the melt and the mode of applied electrolytic current and potential. Carbon films with excellent adhesive property were obtained by PR (periodically reversed) electrolysis method comparing with the film obtained by the other electrolysis method (potentiostatic electrolysis and constant current pulse electrolysis). A two-layered structure of carbon film was identified. The outer part layer of about 1  $\mu\text{m}$  thickness was composed of weakly aggregated carbon particles and the inner part layer of about 0.6  $\mu\text{m}$  thickness was composed of fine and strongly aggregated carbon particles.

*Keywords: cathodic reduction, carbonate ion, carbon-coated layer, molten salt electrochemical process, pulse and PR electrolysis.*

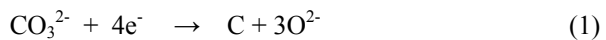
## 1 Introduction

At the present time, carbon coating possessing both high rigidity and low friction coefficient are attracting much attention in the surface technology, in order to

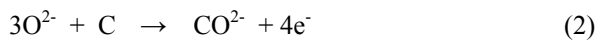


meet the needs to form hard and smooth surface on various materials, which might realize the high precision and high speed mechanical processing. The carbon films possess desirable physical and chemical properties such as high wear resistance, lubricity, electrical conductivity, thermal conductivity, corrosion resistance, heat resistance and so on. In addition, the carbon coating technology is highly demanded to develop lightweight materials used for body parts of automobile cars and airplanes in order for maintaining core toughness with high surface hardness of materials, and for significantly reducing the fuel cost [1]. Furthermore, carbon coated materials are useful for the electrodes of fuel cell, battery and capacitor. It is also useful for the induction heating materials. An amorphous structure of DLC coating can be applied onto bearing metal, drill, cutter and high speed tools for performing unique surface property. This new coating film has a possibility to be widely used not only for automobile materials but even for medical equipments. So far, various carbon coating methods have been proposed and developed. Among them, chemical vapor deposition (CVD) and physical vapor deposition (PVD) are widely used for producing carbon deposited film [2, 3]. The major drawback of vapor deposition method is that they essentially need high-level energy and temperature, which requires expensive instrument and high production cost. And in some cases, poisonous material is used as a raw material. To overcome this kind of difficulty, the authors have proposed a novel procedure for forming carbon film [4]. This method is really an essential one for producing fine carbon film with low manufacturing cost, which is called “molten salt electrochemical process (MSEP)”.

The electrochemical formation of carbon film can be achieved by cathodic reduction of carbonate ions ( $\text{CO}_3^{2-}$ ) in molten salt ( $\text{LiCl-KCl-K}_2\text{CO}_3$ ) [5, 6]. A schematic diagram of carbon film formation is drawn in Fig. 1. When a substrate metal to be treated is cathodically polarized in the  $\text{LiCl-KCl-K}_2\text{CO}_3$  melt, cathodic reduction of  $\text{CO}_3^{2-}$  occurs by the following reaction:



In the case of using graphite rod as an anode, anodic oxidation reaction can be written as follows:



If the insoluble oxygen generating anode is used, the anodic reaction would be limited to only equation (3).

The authors have conducted systematic experimental studies on this cathodic reduction of  $\text{CO}_3^{2-}$  ions, in order to find out the optimal conditions to achieve the most desirable carbon coating.

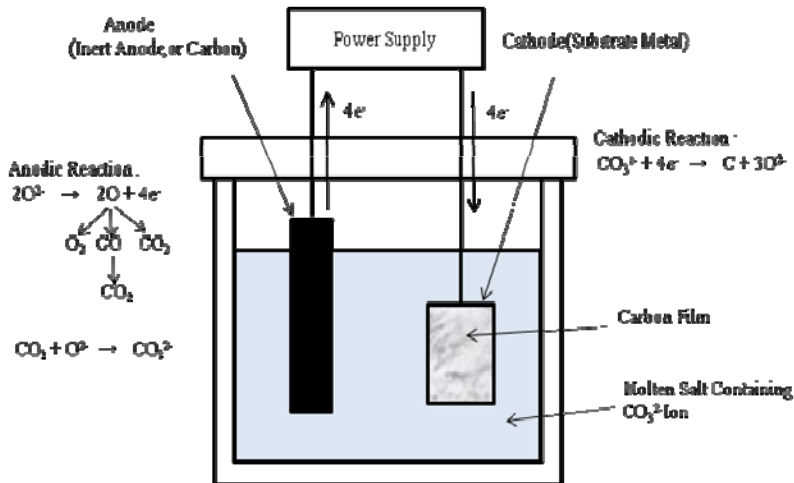


Figure 1: Principle of the electrochemical formation of carbon film by cathodic reduction of carbonate ions.

## 2 Experimental procedures

### 2.1 Experimental apparatus

Figure 2 shows a schematic drawing of the experimental apparatus. In this experiment, an LiCl-KCl eutectic mixture (59:41 mol%) was used as an electrolyte. A silica glass cylindrical container holding alumina-crucible inside was set-up in the electrical furnace. The interior of the furnace was covered by flowed argon gas and the temperature was raised slowly up to 500 or 550°C. The electrolyte was purified by supplying HCl gas to remove water and other impurities in the melt. Then, potassium carbonate ( $K_2CO_3$ ; purity: 99.5%, Wako Pure Chemical Industries, Ltd.) was added directly into the melt as a carbonate ion source.

Electrochemical measurements and electrolyses were conducted using an electrochemical measurement system (HZ-5000, Hokuto Denko Co., Ltd.). Ni wire (1 mm $\Phi$ ) was used as a working electrode of electrochemical measurements (cyclic voltammetry) and austenitic stainless steel (SUS304) plate was used as a working electrode (specimen to be treated) of electrolyses. A carbon rod was used as a counter electrode. The reference electrode was made from a Ag wire which was immersed in a Pyrex glass tube containing a molten salt mixture of LiCl-KCl and a 1 mol% of AgCl. The potential of this electrode was calibrated with reference to that of the  $Li^+/Li$  electrode, which was prepared by electrodepositing Li metal on a Ni wire. All potentials in this paper are given with reference to this  $Li^+/Li$  electrode potential.

SUS304 was used as a specimen, which was first treated by alcoholic base cleaning at 50°C and followed by soaking through 10% of HCl at room temperature. Every sample was degreased and dried clearly before electrolysis.

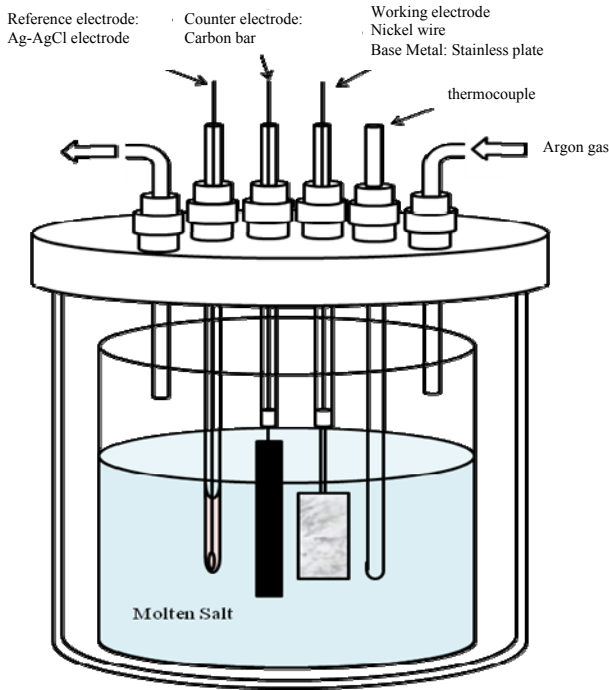


Figure 2: A schematic diagram of the experimental apparatus.

After formation of carbon film for a specified time at the desired temperature, specimen was washed by water, and ultrasonic cleaning was done to remove the salt remaining on the specimen surface. After drying the sample, visual observation and adhesion tape test were conducted to verify the denseness and the adhesiveness of the carbon film.

## 2.2 Constant potential electrolysis

In order to define optimal potential range for making the most desirable carbon film, the effect of electrolysis potential on the carbon coated specimens was investigated. Samples were prepared by potentiostatic electrolyses at various potentials in the potential range where cathodic reduction of  $\text{CO}_3^{2-}$  occurs.

## 2.3 The influence of concentration of $\text{CO}_3^{2-}$ ions

Potentiostatic electrolyses were conducted with various concentrations of  $\text{CO}_3^{2-}$  ions (1 to 5 mol%  $\text{K}_2\text{CO}_3$  added).

## 2.4 The influence of temperature of the melt

Operating temperatures were selected at 500 and 550°C and the effect of the temperature on the formed carbon film was investigated.

### 2.5 Constant current pulse electrolysis and periodically reversed electrolysis

The applicability of the constant current pulse electrolysis and periodically reversed (PR) electrolysis were examined. The morphology of the carbon film was observed by a metallurgical microscope and a SEM (scanning electron microscope).

## 3 Results and discussion

Figure 3 shows typical cyclic voltammogram for Ni electrode after adding 5 mol%  $K_2CO_3$  into the LiCl-KCl melt at  $500^\circ C$ . Cathodic currents were observed at potentials more negative than 1200 mV. Potentiostatic electrolyses were conducted at the potentials between 0 to 1300 mV. Photographs of specimens after electrolyses are shown in Fig. 4. Carbon film was observed at each potential more negative than 1200 mV (even at 0 mV) and was not observed at 1300 mV. It has been estimated that the reduction currents at potentials more negative than 1200 mV are considered to correspond to the reaction of eqn (1). When electrolyses were conducted at more negative potentials than 500 mV, bubble generation was observed during rinsing the specimens in water. It indicates that Li metal formed during electrolysis was remained in the carbon layer or melt at specimen surface.

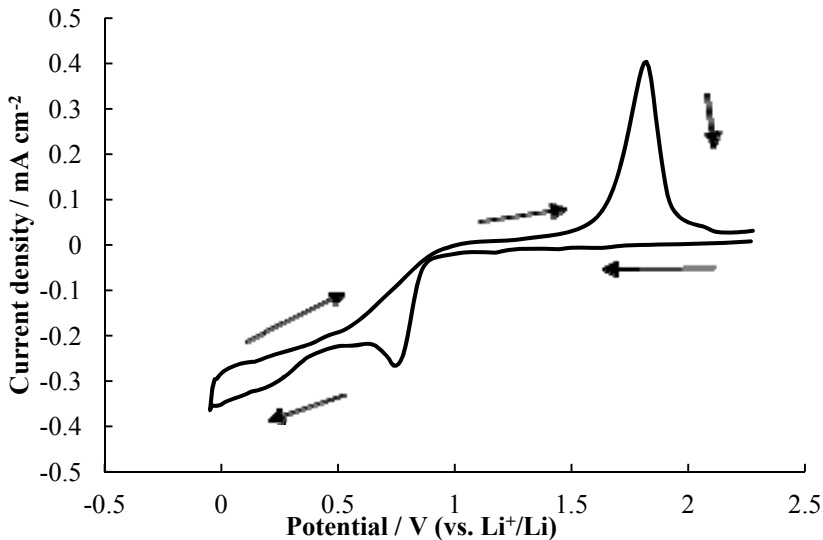


Figure 3: Cyclic voltammogram for Ni electrode after adding 5 mol%  $K_2CO_3$  into the LiCl-KCl melt at  $500^\circ C$ . Scan rate: 10 mV/sec.









Potential (mV)	0	300	500	700
Sample				
Potential (mV)	900	1000	1100	1300
Sample				

Figure 4: Photographs of samples after potentiostatic electrolysis at various potentials ( $K_2CO_3$ : 4 mol%, Temperature: 500°C).

Figures 5 and 6 show cyclic voltammograms for Ni electrode after adding 1 to 5 mol%  $K_2CO_3$  into the LiCl-KCl melt at 500 and 550°C, respectively. They clearly indicate that the cathodic reduction current was increased with the increase of the amount of  $K_2CO_3$  at both of the selected temperature. Carbon films with excellent adhesive property were obtained by potentiostatic electrolysis at 700 mV in the melt with 3-5 mol%  $K_2CO_3$  at 550°C, which is shown in Fig. 7. However, at each temperature, the remaining  $K_2CO_3$  was observed at the surface of the melt after adding 5 mol%  $K_2CO_3$ . Therefore, in subsequent experiments, the added amount of  $K_2CO_3$  was fixed as 4 mol%.

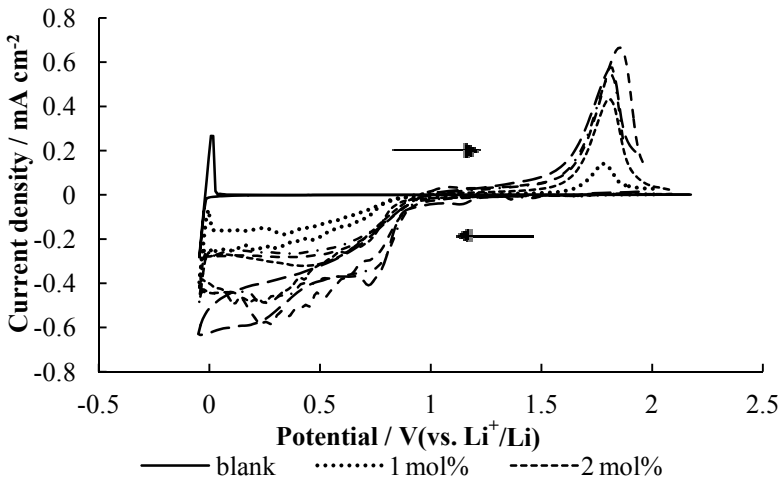


Figure 5: Cyclic voltammogram for Ni electrode before and after adding 1 to 5 mol%  $K_2CO_3$  into the LiCl-KCl melt at 500°C. Scan rate: 10 mV/sec.

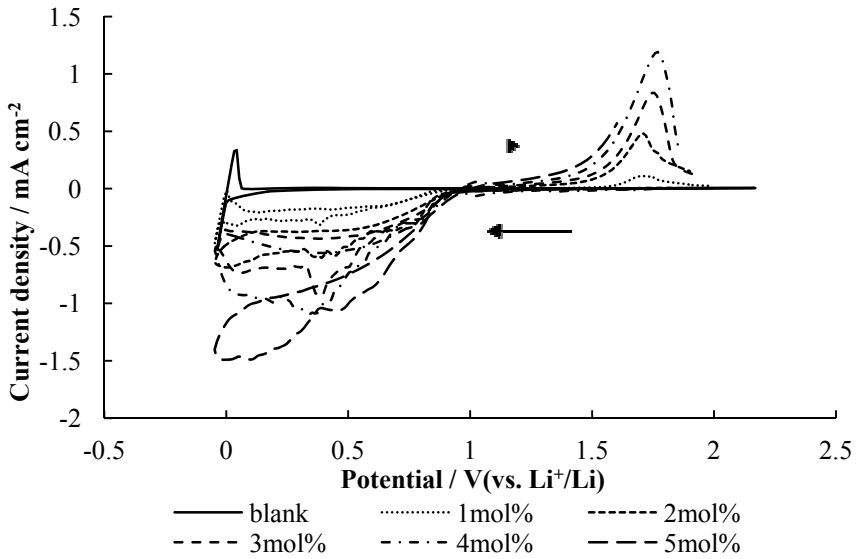


Figure 6: Cyclic voltammogram for Ni electrode before and after adding 1 to 5 mol% K<sub>2</sub>CO<sub>3</sub> into the LiCl-KCl melt at 550°C. Scan rate: 10 mV/sec.

	1 mol%	2 mol%	3 mol%	4 mol%	5 mol%
500°C					
550°C					

Figure 7: Photographs of samples after potentiostatic electrolysis at 700 mV in various concentrations of K<sub>2</sub>CO<sub>3</sub> at 500°C.

Subsequently, potentiostatic electrolyses were conducted at the potentials 700 and 900 mV in the 4 mol%  $K_2CO_3$  added melt at 500 and 550°C. Photographs of specimens after electrolyses are shown in Fig. 8. Carbon films were observed on the all specimens, but films made at 500°C were partly removed during rinsing in water. Carbon films made at 550°C showed more excellent adhesive property than that made at 500°C. However, these films were also removed when ultrasonic cleaning was conducted.

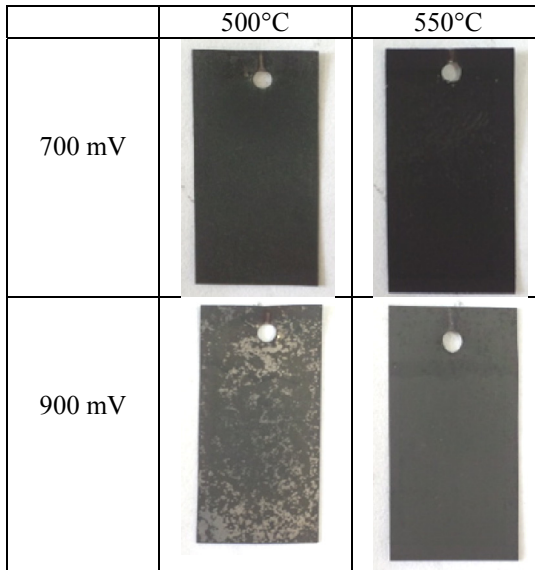


Figure 8: Photographs of samples after potentiostatic electrolysis at 700 and 900 mV at 500 and 550°C ( $K_2CO_3$ : 4 mol%).

In order to obtain carbon films with excellent adhesive property, the constant current pulse electrolysis and periodically reversed (PR) electrolysis were conducted in the 4 mol%  $K_2CO_3$  added melt at 550°C. As a result of pulse electrolysis, a very dense and smooth plating layer is formed without adding any leveling ingredients [7]. PR electrolysis is the electrolysis method which changes the direction of current periodically for a certain period of time. Undesirable substances accumulated or formed on the surface during the cathodic electrolysis period are removed during anodic electrolysis. As a result, a fine adhesive layer is formed after PR electrolysis [7].

Figure 9 shows surface microstructures of the carbon layer obtained by each electrolysis method after ultrasonic cleaning. It shows that a black deposited layer is obtained by the application of constant current pulse electrolysis. A large portion of these layers were stripped out during the rinsing in water and later ultrasonic cleaning.



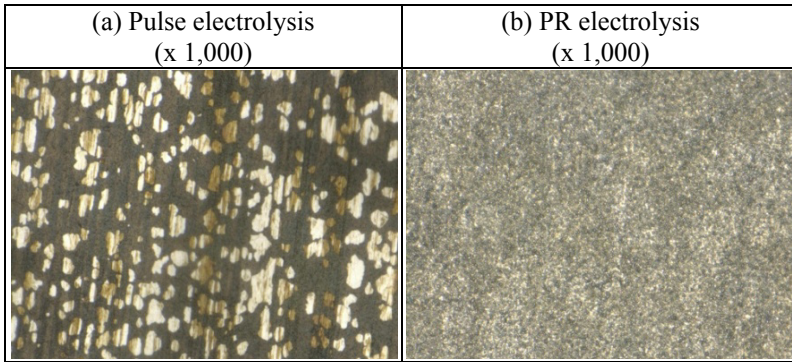


Figure 9: Surface microstructures of the carbon film obtained by (a) constant current pulse electrolysis and (b) periodically reversed (PR) electrolysis after ultrasonic cleaning.

Carbon films with more excellent adhesive property were obtained by the PR electrolysis method comparing with other electrolysis method. An adhesive thick layer was observed even after the ultrasonic cleaning. The color of the carbon film was somewhat dull grayish. Figure 10 shows SEM images (a: surface, b: cross-sectional) of the carbon film. In the SEM images, two-layered structure of carbon film was identified. The outer part layer of about 1  $\mu\text{m}$  thickness was composed of weakly aggregated carbon particles and the inner part layer of about 0.6  $\mu\text{m}$  thickness was composed of the fine and strongly aggregated carbon particles. Especially in the early period of electrolysis, it is considered that a dense layer was formed due to the effect of PR electrolysis.

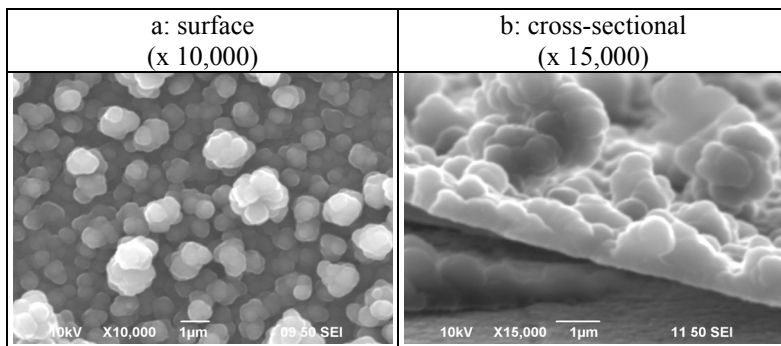


Figure 10: SEM images (a: surface, b: cross-sectional) of the carbon film obtained by PR electrolysis.

## 4 Conclusion

Formation of carbon film by the cathodic reduction of  $\text{CO}_3^{2-}$  ions in molten salt was investigated under various different electrolysis conditions, such as concentration of  $\text{CO}_3^{2-}$  ions, temperature of the melt and the mode of applied electrolytic current and potential. Carbon films with much more excellent adhesive property were successfully obtained by PR (periodically reversed) electrolysis method comparing with the film obtained by the other electrolysis method (potentiostatic electrolysis and constant current pulse electrolysis). The formation of two-layered structure of carbon film was identified. The outer part layer of about 1  $\mu\text{m}$  thickness was composed of weakly aggregated carbon particles and the inner part layer of about 0.6  $\mu\text{m}$  thickness was composed of fine and strongly aggregated carbon particles.

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