



THE ELECTROLYTIC DEPOSITION OF CARBON FROM MOLTEN Li_2CO_3



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Abstract: Electrodeposition of carbon on an nickel electrode in molten salt has been investigated with the aid of scanning electron microscopy (SEM) and cyclic voltammetry, using molten LiCl , as a base electrolyte with adding of 1 and 5 % of Li_2CO_3 . Commercial nickel wire was used as a cathode and graphite crucible as the anode electrode. A cyclic voltammograms for an nickel electrode indicates that the deposition or discharge of carbon at the cathode occurs at potential range of - 0.8 to -1.7 V. Further, SEM observations showed that morphology of the carbon at the cathode is in the form of a fairly hard black deposit. It was found that the quality of the deposit depends by the cathode surface, applied overpotential, content of lithium carbonate and the thickness of the carbon film.

Key words: electrodeposition, carbon film, nickel electrode, molten salts,

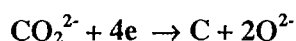
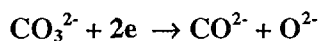
1. INTRODUCTION

Currently carbon is used as an anode material in several electrochemical processes, due to its properties such as high heat resistance, corrosion resistance in oxidation conditions and low cost. If a cohesive carbon film on a metal substrate is obtained, the corrosion resistance and/or thermal resistance of the surface of the metal substrate may be greatly improved because the corrosion resistance or thermal resistance of carbon is superior to that of metal.

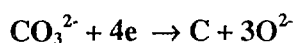
The standard method for preparing carbon films is chemical vapour deposition (CVD), but it is very expensive because of the high temperatures involved (1500 °C). Thus, electrodeposition of carbon on usual substrates such as cooper, nickel could be a promising alternative, because of the lower temperature of the process.

Several authors [1- 4,] have reported the formation of carbon films by electrolysis in molten salts. Two different mechanisms have been proposed for the electroreduction of these ions:

1. The first mechanism is two steps reduction of carbonate CO_3^{2-} ions into carbon



2. The second mechanism in one step reduction of carbonate CO_3^{2-} ions into carbon



This work presents a study of the electrochemical reduction of carbonate CO_3^{2-} ions into carbon in $\text{LiCl-Li}_2\text{CO}_3$ media at a temperature of 700 °C. Finally, some carbon deposits were obtained on a nickel electrode.

2. EXPERIMENTAL

The experiments were carried out in a cylindrical graphite cell (external: 15.0 cm height and 9.0 cm diameter; internal: 14.0 cm height and 7.0 cm diameter, Graphite Technologies, high density grade) as the container of the molten salt electrolyte. The crucible served as the anode while a nickel wire was inserted into the electrolyte (1.0 mm diameter) to act as a cathode. 20 mm in length of the cathode was exposed to the electrolyte to give an initial cathodic surface area of 0.07 cm². The cathode was



surrounded with to a ceramic sheath, to prevent electrical contact between the cathode and anode which can be caused by floating of lithium on the surface of the electrolyte. In these experiments $\text{LiCl} + \text{Li}_2\text{CO}_3$ salt was used at a temperature of 700°C .

The cell was used inside a sellable Inconel tube reactor with a water cooled jacket and heated by a vertical 1600°C Lenton furnace which was equipped with a programmable controller (see Fig. 1). The salt was always thermally pre-dried in an argon atmosphere inside the Inconel tube at 250°C for at least 2 h and was then melted in an argon atmosphere. The electrolysis was controlled by a Farnell LS30-10 autoranging power supply. The cathode was inserted into the melt, deposited and after the electrolysis time lifted above the salt inside the tube and left to cool under inert atmosphere below 100°C .

After each experiment, the cathode was removed and washed with water and 1 M HCl. The deposits were inspected by electron microscopy, using JEOL 6340F (SEM, 10 kV),

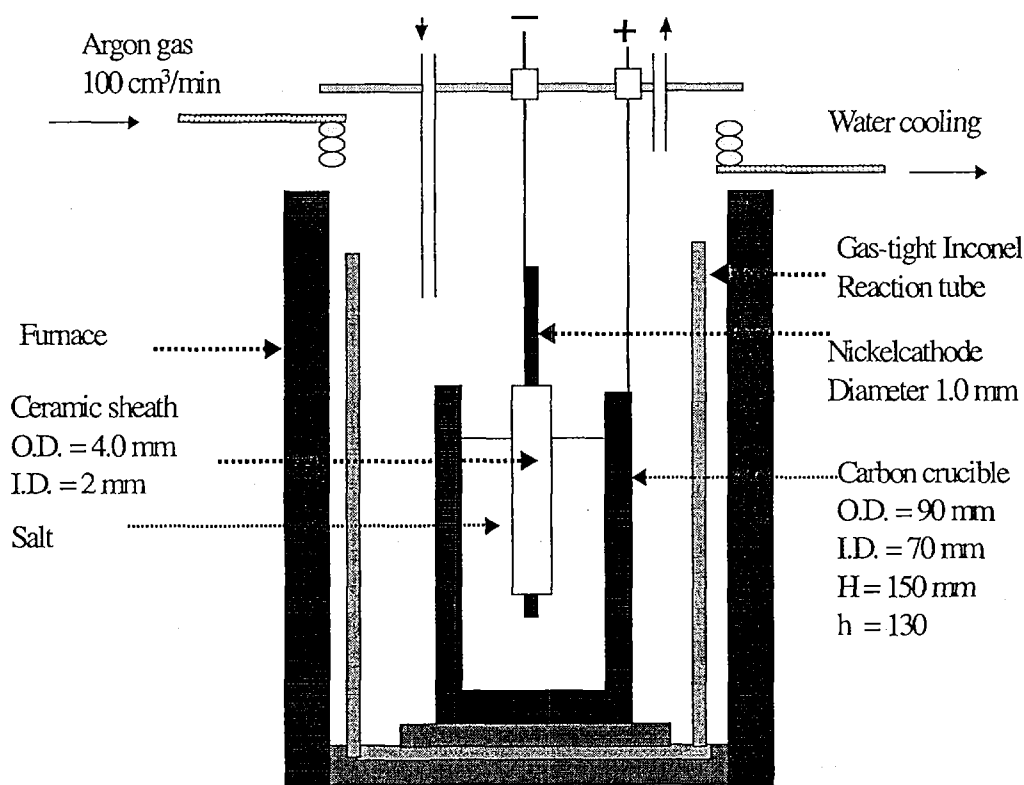


Fig. 1. A schematic diagram of the experimental set-up for molten salt electrodeposition.

3. RESULTS AND DISCUSSION

3.1. CYCLIC VOLTAMETRY

Cyclic voltammetry is often the first experiment performed in an electrochemical study on a material used as an electrode. For that reason, before the process of electrolysis was done, some curves were recorded for each system.

The polarization curves obtained at a scan rate of 100 mV/s in pure molten LiCl , as a base electrolyte and $\text{LiCl} + 1\%$ and 5% of Li_2CO_3 by weight, on a nickel wire, are shown in Figs. 2, 3 and 4. It is



obvious that metallic lithium deposition or reduction, figure 2, on the nickel electrode occurs at a potential of -1.9 V at 700 °C.

The voltammogram shown on figures 2 and 3, shows that the electrochemical reactions occurs as a result of quantity of added lithium carbonate is completely different from that occurring in pure lithium salt [2]. It is obvious, from the voltammogram, that 1% and 5 % of lithium carbonate added in the melt, exhibits the occurrence of some other electrochemical process at the cathode. This means that some early electrochemical reaction starts at a potential of around -0.8 V. This early cathode reaction probably occurs as a result of carbon discharge at this potential.

The curves clearly illustrate that addition of carbonate causes marked changes in the experimentally obtained voltammograms[2,5]. This suggests the occurrence of an early electrochemical reduction process. The process has a cathodic current peak or plateau at approximately -0.8 to -1.7 V that is directly proportional to the added concentration of Li_2CO_3 .

It is worth emphasizing that the cyclic voltammograms presented in figures 3, 4 and 5, confirm that discharge of carbon is the first electrochemical step to occur in the process.

3.2. ELECTRODEPOSITION OF CARBON

The preceding results show that the reduction of CO_3^{2-} ions occurs in potential range of -0.8 to -1.7 V. In order to confirm the reaction around this potential, and characterize the electrolytic carbon deposits obtained, some potentiostatic electrolysis runs were carried out at a potential of -1.3 V and temperature of 700 °C on nickel electrodes. The electrolysis time was limited at 30 and 60 seconds.

The morphology of the deposits obtained under the conditions presented above are shown at Figs.5 and 6. From SEM images of the surface of the carbon deposit it seems that the whole surface of the nickel is covered.

Furthermore, Fig. 5, shows that the morphology of the deposit or the film formed at the cathode surface is quite smooth. The observation shows that after the cooling of the cathode at the surface a thick mixed film of carbon and salt is formed. To avoid this problem the method of washing and the solution were changed. The next samples were washed with 1M HCl in ultrasonic bath. Obtained results are shown at Fig. 6. SEM image presented on Fig. 6 show, that the new method used for washing successfully removes the salt from the surface. This confirms that the thin film was formed by the salt due to raising of the nickel wire from the electrolyte.

It is obvious (Fig. 6), that the whole surface is covered with carbon deposit, but the morphology of this deposit is different than previous one. The surface looks like polycrystalline deposit and is not smooth as a previous one.

The observation of the samples shows that the differences between them are caused after the electrolysis during the cooling time and also because of a methods used for washing.

It is also worth to mention that this deposit is formed inside the crucible, during the process of electrolysis at the temperature of 700 °C.

Notice that in these experimental conditions, the salt included in the deposit can be removed only by washing of the deposit with solution of 1M HCl in an ultrasonic bath. It seems that the washing off the deposit decreases somewhat the adherence of electrodeposited carbon.

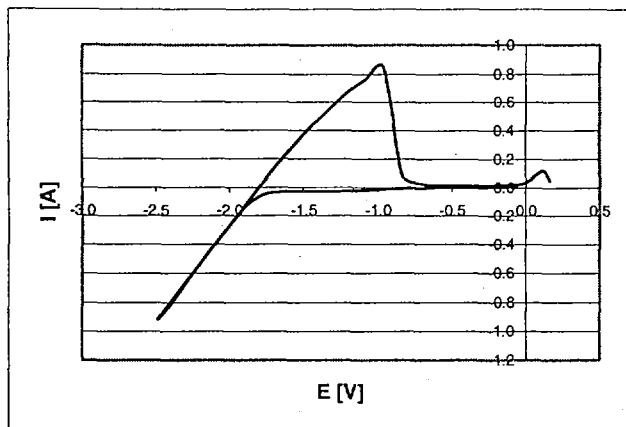


Fig.2. Cyclic voltamogram for a nickel electrode in molten LiCl at a scan rate of $v = 100 \text{ mV/s}$ at $700 \text{ }^\circ\text{C}$.

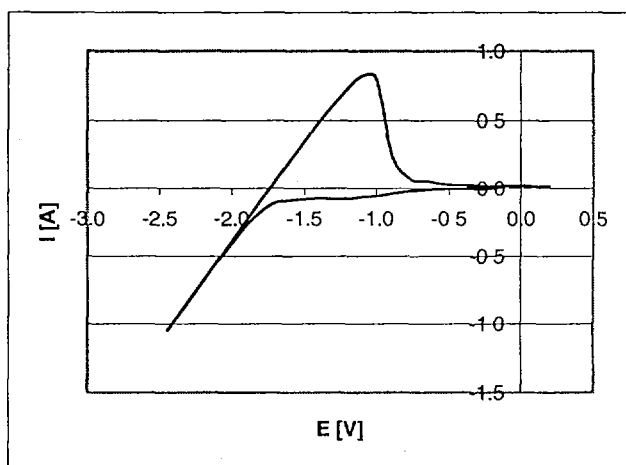


Fig.3. Cyclic voltamogram for a nickel electrode in molten 99% LiCl + 1% Li_2CO_3 at a scan rate of $v = 100 \text{ mV/s}$ at $700 \text{ }^\circ\text{C}$.

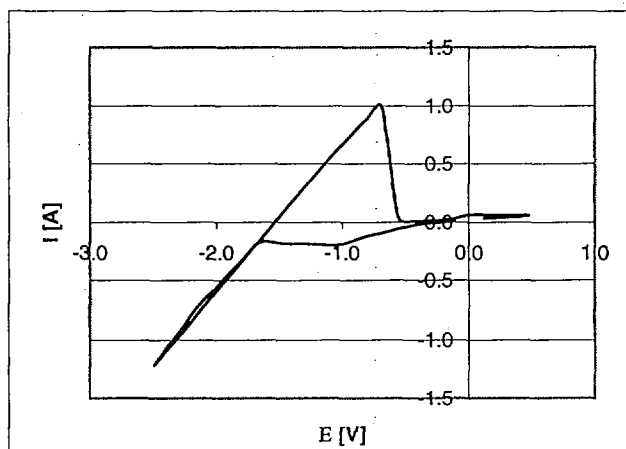


Fig.4. Cyclic voltamogram for a nickel electrode in molten 95% LiCl + 5% Li_2CO_3 at a scan rate of $v = 100 \text{ mV/s}$ at $700 \text{ }^\circ\text{C}$.

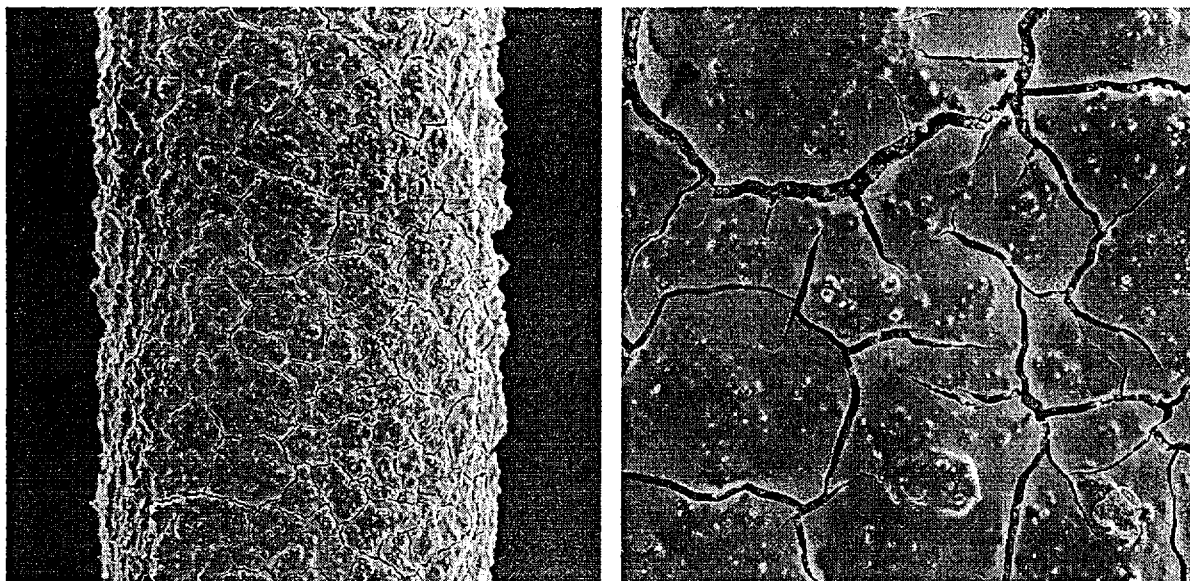


Fig. 5. SEM images of Carbon film obtained potentiostatically on nickel wire in molten $\text{LiCl} + 5\% \text{Li}_2\text{CO}_3$ at temperature of 700°C . The film is washed with water. Magnification: a) 100x and b) 500x. Time of deposition 30 seconds. Overpotential $\eta = -1.3 \text{ V}$.

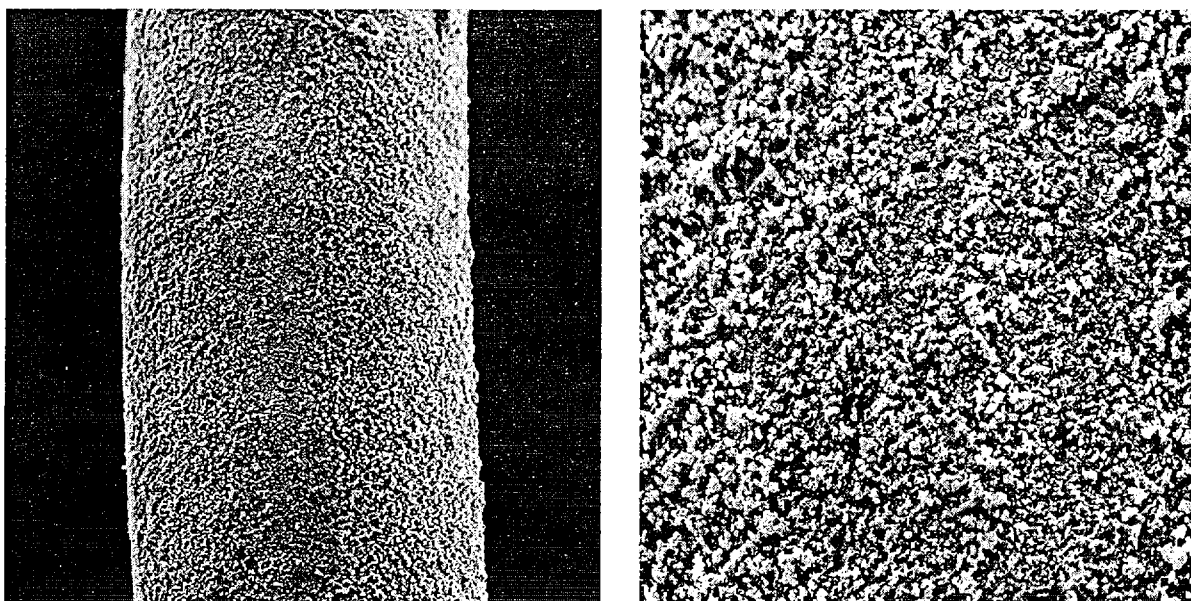


Fig. 6. SEM images of Carbon film obtained potentiostatically on nickel wire in molten $\text{LiCl} + 5\% \text{Li}_2\text{CO}_3$ at temperature of 700°C . The film is washed with 1M HCl . Magnification: a) 100x and b) 500x. Time of deposition 30 seconds. Overpotential $\eta = -1.3 \text{ V}$.



4. SUMMARY

From the results presented in this work, we can summarize:

- Carbon films can be prepared by electrochemical reduction of carbonate ions in molten $\text{LiCl} + \text{Li}_2\text{CO}_3$,
- The obtained carbon is in the form of fairly hard black deposit and fairly good adherence at the substrata. It was found also that the deposit is mixed and covered with low quantity of solidified salt.
- The salt formed at the surface can be removed with washing. The best solution for washing is 1M HCl,

A further investigation will concern the influence of the experimental conditions (temperatures, current density or potential applied) on the morphology of the carbon deposits correlated with an investigation on the appearance and growth of the layer

Acknowledgment

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