

ELECTROCHEMICAL STUDY OF THE ELECTRODEPOSITION AND INTERCALATION OF SODIUM INTO GRAPHITE FROM SODIUM CHLORIDE AS THE FIRST STEP OF CARBON NANO-TUBES FORMATION

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Abstract

The mechanism of sodium reduction in sodium chloride melt at three different electrodes has been investigated by means of cyclic voltammetry. The definition of so-called 'thermodynamic' or 'material balance' reversibility has been introduced. It has been shown that the dissolution of sodium in the melt is an important factor in the overall process in the whole range of polarization rates. The adsorption of sodium on glassy carbon and graphite plays an important role in the reduction of sodium at polarization rates below 1 V/s, and it makes the process reversibility higher compared to molybdenum. The intercalation of sodium into the graphite lattice decreases the overall reversibility of the process at low polarization rates.

Keywords: sodium chloride, sodium, deposition, intercalation, reversibility,
carbon nano-tubes

1. Introduction

Carbon nano-tubes were discovered in 1991 [1] and since then different techniques to obtain them have been studied. One of the possibilities is to produce carbon nano/micro-tubes by electrochemical synthesis from molten salts using graphite cathode and a salt from which an alkali or alkaline earth metal can be deposited on the surface

of the cathode [2-8]. According to our present understanding, the deposited alkali (*Li*, *Na*) or alkaline earth (*Mg*, *Ca*) metal atoms intercalate into the space between the graphite planes causing mechanical stress, and part of the depleting graphite planes appear to be in the form of carbon tubes [9-10]. The typical diameter of those tubes ranges from 2 nanometers to 20 micrometers with a length being much larger than the actual diameter.

According to our preliminary studies, *LiCl*, *NaCl*, *MgCl₂* and *CaCl₂* seem to be suitable molten salts for nano-tube synthesis [11]. The reason for that is that by electrolyzing these salts (or their mixtures) *Li*, *Na*, *Mg* or *Ca* atoms, which are all capable of intercalating in between the graphite planes, can be deposited on a graphite cathode. The goal of this study is to gain some understanding on the mechanism of intercalation and thus nano-tube formation. For this series of experiments we have chosen the simplest possible system, pure sodium chloride. In order to ‘catch’ the electrochemical signature of the intercalation process, the comparative electrochemical analysis of the following three working electrodes was performed by cyclic voltammetry:

- i. molybdenum, having practically zero mutual solubility and no compound formation tendency with *Na* (or with *NaCl*), and thus serving as a ‘reference’ inert electrode;
- ii. glassy carbon, providing carbon sites for the deposited sodium, but not allowing intercalation of *Na* into its bulk – thus, the glassy carbon electrode can be considered as an ‘intermediate reference’ electrode between molybdenum and graphite electrodes;
- iii. graphite electrode, being the target material of our investigation.

2. Experimental

Experiments were performed using a three-electrode electrochemical cell. The working electrodes (WE) were a molybdenum wire (0.9 mm diameter, 0.29 cm² of active surface), glassy carbon rod (1.8 mm in diameter, 0.20 cm² of active surface) and graphite rod (3 mm in diameter, 0.47 cm² of active surface) in different experiments. The reference electrode was a molybdenum wire (0.9 mm in diameter).

A glassy carbon crucible was used as container for the electrolyte and also as the auxiliary electrode. The electrochemical experiments were carried out in a water-cooled nickel super-alloy reactor, placed inside a vertical tube furnace.

Sodium chloride was placed in the glassy carbon crucible and flushed with dry *Ar* at room temperature. The salt was heated up to 120 °C in vacuum and held at this conditions for around 40 h. After that the salt has been slowly heated up to 300 °C, flushed with dry *Ar*, vacuumed and held at this temperature for 1h. Then, the salt was heated up to the working temperature of 850 °C in dry *Ar*, and held at this temperature over 1h, before starting the measurements. The electrochemical measurements were

conducted by a computer-controlled potentiostat VoltaLab PGZ 301.

As sodium is known to dissolve in sodium chloride [12], special care was taken to obtain reproducible and comparable results on all electrodes. Voltammetric curves were started at +0.2 V, conducted to the break potential (it varied from 0 to -2.0 V in different CV runs) and then reversed back to +0.2 V. The range of polarization rates was from 0.01 to 20 V/s. Mathematical treatment of the curves obtained has been performed by means of the VoltaMaster 4 (version 5.1) software package.

3. Results and discussion

Some characteristic voltammograms recorded at polarization rates of 10 V/s, 1 V/s and 0.1 V/s on the 3 working electrodes at a break potential of -1.5 V are presented in Figures 1-9. For the first look at the voltammograms, it is obvious that the anodic charge transfer is much less than the cathodic charge transfer. In other words, part of the deposited metal is not oxidized back in the same amount in the anodic cycle. This can be due to the escape of metallic sodium from the cathode surface due to its diffusion to the bulk of the electrolyte or to the bulk of the cathode, i.e. due to its intercalation into graphite.

The "loop" in Fig. 3 (the current after potential reversal until approximately -1.3 V has more negative values than before potential reversal) may be due to the formation of a new phase (that is, sodium metal). This assumption is supported by quite a high value of the quantity of electricity (2.934 Coulomb) passed through the system when taking the curve.

The loops in Figs. 4 and 7 can be explained in the following way. At high polarization rates (1 V/s and higher) the system cannot follow the changes in the working electrode potential, which means that sodium ions cannot momentarily change the movement direction when the polarization is reversed. So for some time after the polarization is reversed we have increasing by absolute value flux of sodium ions, which causes the loop to appear. The higher is the polarization rate and the more negative is the break potential, the more pronounced this effect becomes.

The "wavy" appearance of the curve in Fig. 9 may be due to changes in the surface state of the working electrode because this curve was taken in the middle of the experiment and significant amounts of sodium might have adsorbed/desorbed on the electrode surface or, intercalated into the graphite lattice.

The reversibility of Na deposition/dissolution in a thermodynamic sense is evaluated by us on a 100 % scale by comparing the areas under the anodic and cathodic waves according to the following equation:

$$\text{Rev} = 50 \cdot \left(1 - \frac{A_{\text{anod}}}{A_{\text{cathod}}} \right), \% \quad (1)$$

where A_{anod} and A_{cathod} are areas measured under the anodic and cathodic waves of a voltammogram (the area is negative in the cathodic part of the current and positive in the anodic part of the current).

The physical sense of Eq.(1) is clear from considering the following simple cases:

- i. when the cathodic and anodic waves are identical, i.e. $A_{cathod} = A_{anode}$, i.e. none of the deposited metal is oxidized back, then $Rev = 0$, meaning that the process is fully irreversible and that all the deposited metal is 'lost';
- ii. when the total integral under the anodic wave is zero (i.e. half of it is in the cathodic, while half of it is in the anodic current interval), $Rev = 50\%$, meaning that half of the deposited metal is 'lost';
- iii. when the anodic wave fully compensates the cathodic wave, i.e. $A_{cathod} = -A_{anod}$, $Rev = 100\%$, the process is fully reversible, meaning that all the deposited metal is oxidized back, i.e. there is no metal 'loss' at all.

Table 1. Values of reversibility for the deposition/dissolution of Na in Fig-s 1-9, according to Eq.(1)

Electrode	ν , V/s	E_1 , V	E_2 , V	A_{cath} , mW/cm ²	A_{anod} , mW/cm ²	Rev , %
Molybdenum	10	+0.2	-1.5	-214.0	0.8	50
	1	+0.2	-1.5	-114.8	-11.1	45
	0.1	+0.2	-1.5	-93.9	-89.2	2
Glassy carbon	10	+0.2	-1.5	-1521.9	57.8	52
	1	+0.2	-1.5	-787.8	134.6	59
	0.1	+0.2	-1.5	-356.3	69.7	60
Graphite	10	+0.2	-1.5	-762.2	502.6	83
	1	+0.2	-1.5	-375.5	288.6	88
	0.1	+0.2	-1.5	-146.5	45.8	66

ν - polarization rate,

E_1, E_2 - potentials of scan reverse in the cathodic and anodic part of voltammograms, respectively.

In Fig-s 10-12, the reversibility parameter Rev is shown based on the computer analysis of all the measured curves. From Fig-s 10-12 one can make the following conclusions:

- i. for the *Mo* working electrode the $Rev - \log \nu$ curves have an S-shape form. The majority of curves tend to about $Rev = 50\%$ at $\nu > 1$ V/s, and tend to about $Rev = 0\%$ at $\nu < 0.1$ V/s. This behavior can be explained by fast diffusion of deposited *Na* into bulk *NaCl*. When the polarization rate is very slow, almost 100% of *Na* is able to escape from the electrode surface, and almost none of the deposited *Na* is oxidized back in the anodic cycle. However, when the rate of polarization is large, only the part of sodium deposited in the cathodic cycle is 'lost' by diffusion, and the part of sodium deposited in the beginning of the anodic cycle is actually oxidized back in the end of the anodic cycle.

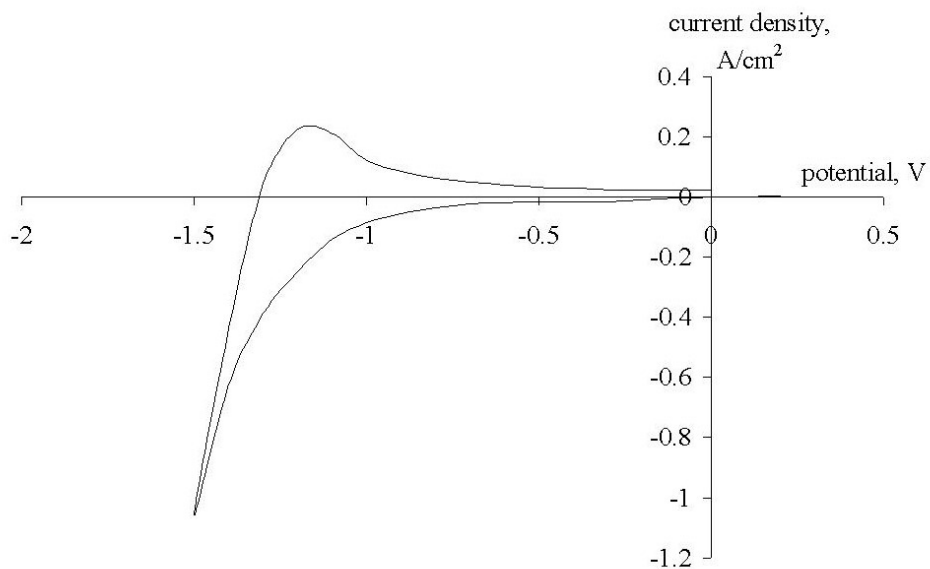


Fig. 1. Cyclic voltammogram recorded on a Mo electrode at a break potential of -1.5 V (Reference electrode - Mo). Polarization rate - 10 V/s , pure NaCl at $850\text{ }^\circ\text{C}$.

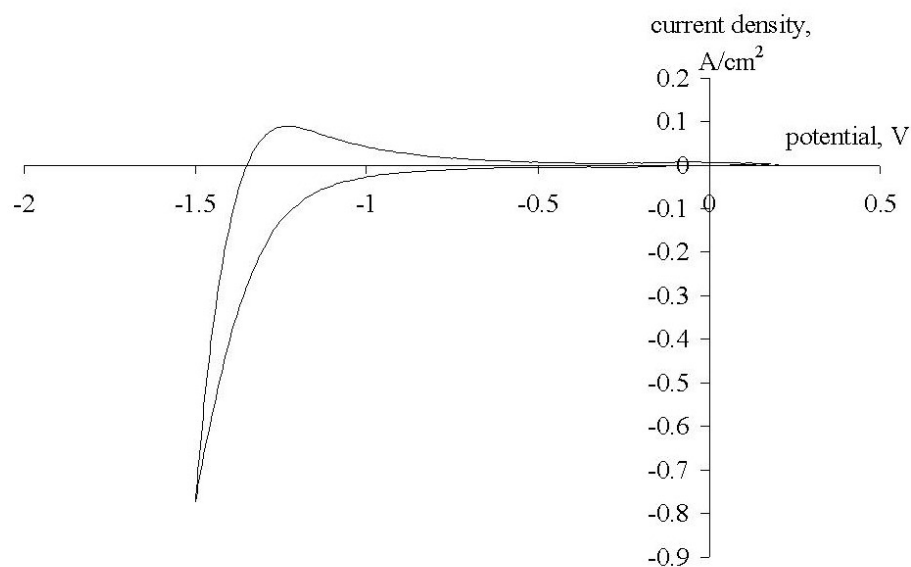


Fig. 2. Cyclic voltammogram recorded on a Mo electrode at a break potential of -1.5 V (Reference electrode - Mo). Polarization rate - 1 V/s , pure NaCl at $850\text{ }^\circ\text{C}$.

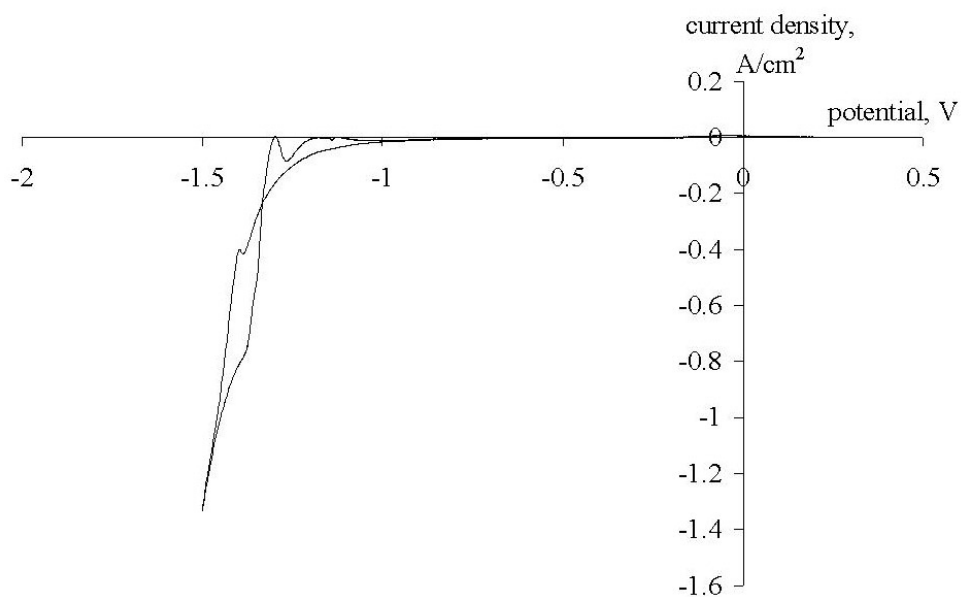


Fig. 3. Cyclic voltammogram recorded on a Mo electrode at a break potential of -1.5 V (Reference electrode - Mo). Polarization rate - 0.1 V/s, pure NaCl at 850 °C.

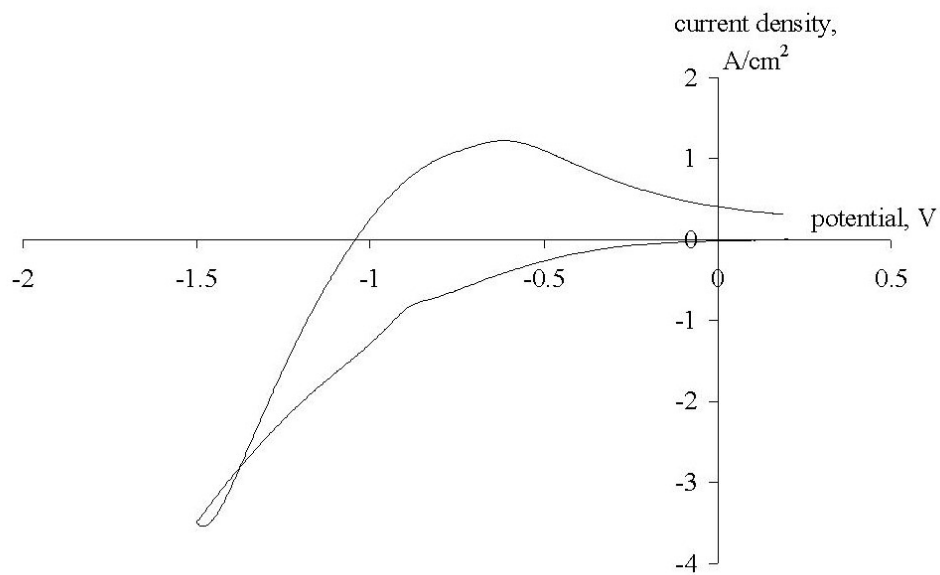


Fig. 4. Cyclic voltammogram recorded on a GC electrode at a break potential of -1.5 V (Reference electrode - Mo). Polarization rate - 10 V/s, pure NaCl at 850 °C.

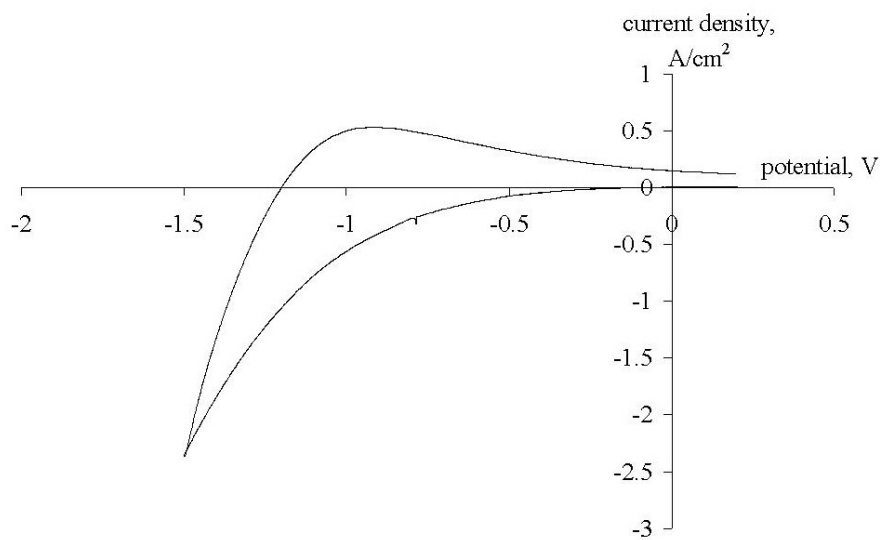


Fig. 5. Cyclic voltammogram recorded on a GC electrode at a break potential of -1.5 V (Reference electrode - Mo). Polarization rate -1 V/s , pure NaCl at $850\text{ }^\circ\text{C}$.

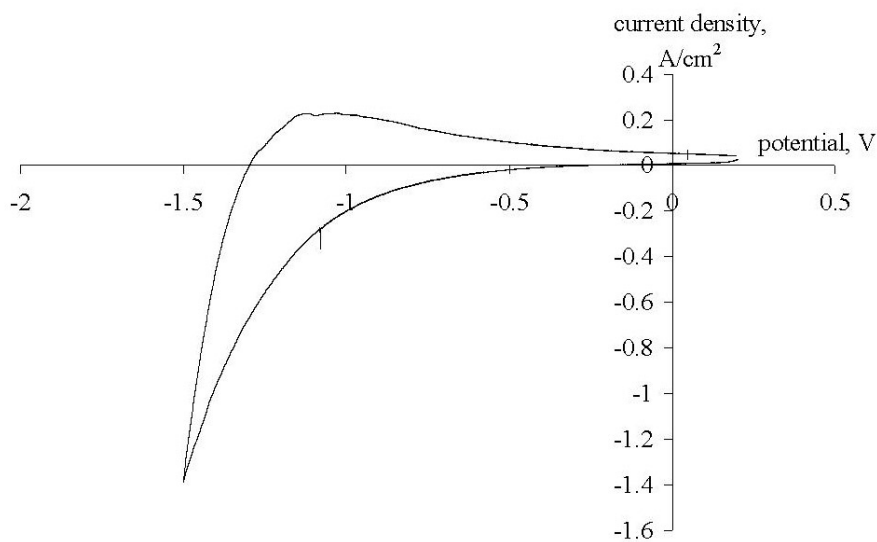


Fig. 6. Cyclic voltammogram recorded on a GC electrode at a break potential of -1.5 V (Reference electrode - Mo). Polarization rate -0.1 V/s , pure NaCl at $850\text{ }^\circ\text{C}$.

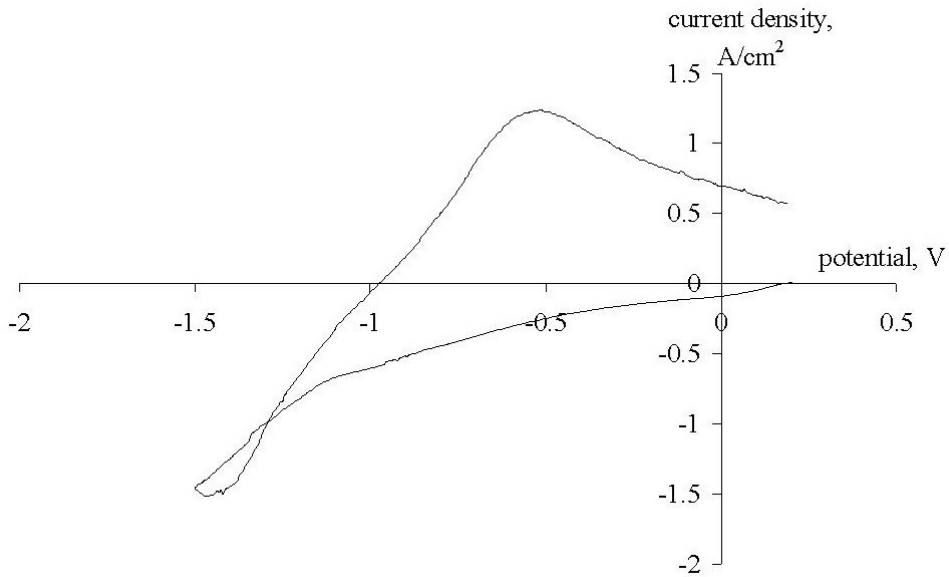


Fig. 7. Cyclic voltammogram recorded on a graphite electrode at a break potential of -1.5 V (Reference electrode - Mo). Polarization rate - 10 V/s, pure NaCl at 850 °C.

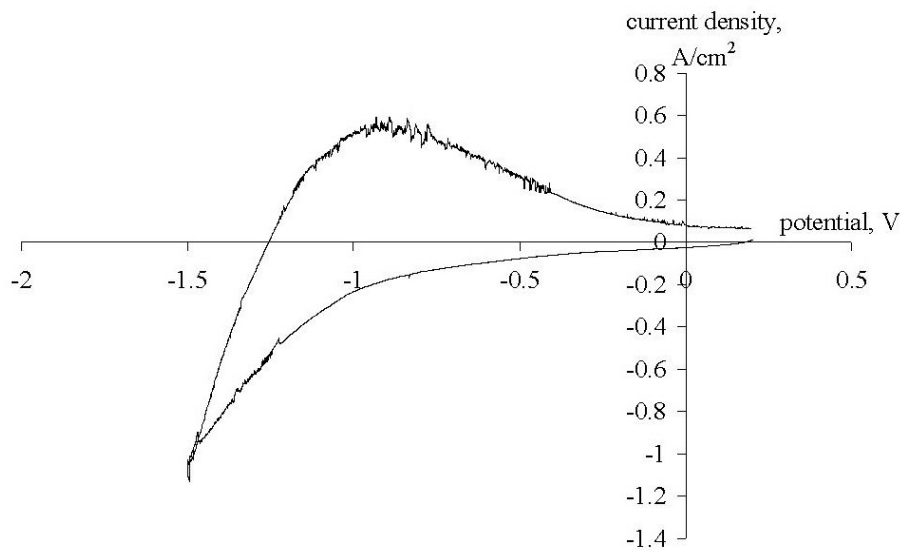


Fig. 8. Cyclic voltammogram recorded on a graphite electrode at a break potential of -1.5 V (Reference electrode - Mo). Polarization rate - 1 V/s, pure NaCl at 850 °C.

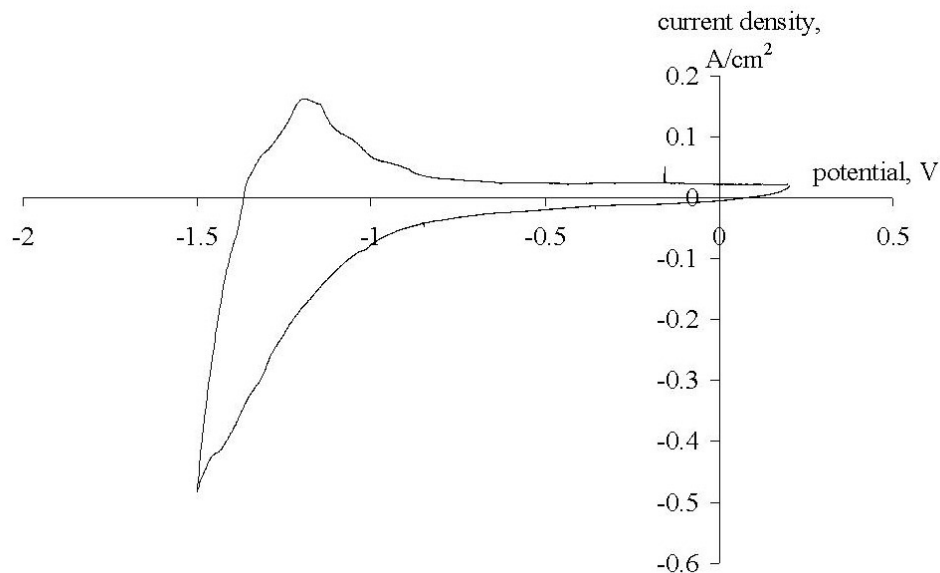


Fig. 9. Cyclic voltammogram recorded on a graphite electrode at a break potential of -1.5 V (Reference electrode - Mo). Polarization rate - 0.1 V/s, pure NaCl at 850 °C.

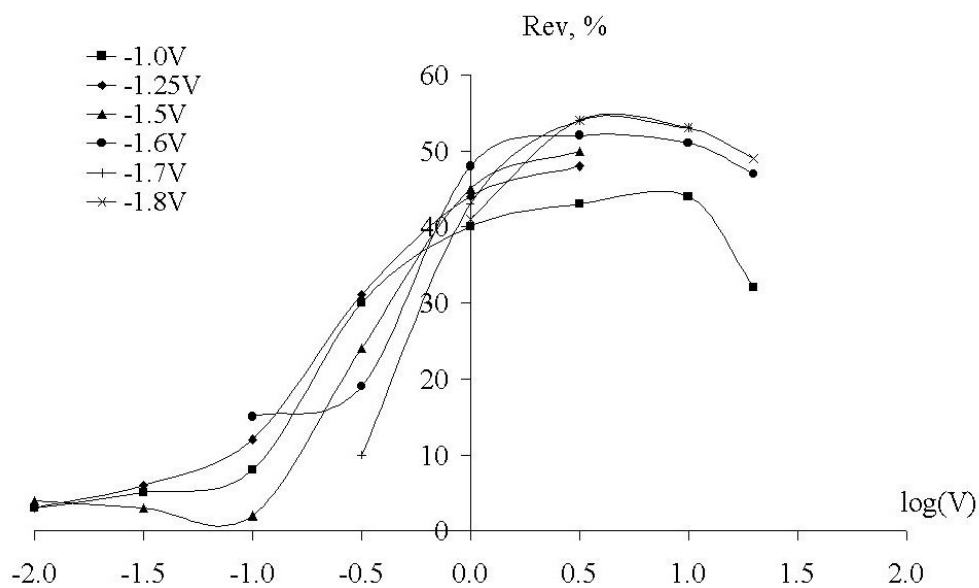


Fig. 10. Reversibility parameter Rev as a function of polarization rate (semi-logarithmic scale) at different break potentials (Reference electrode - Mo) measured on a Mo electrode in pure NaCl at 850 °C.

ii. for the GC working electrode the Rev values have approximately the same 50 %, or a bit higher (60 %) value at the largest rate of polarization (20 V/s). However, with decreasing the polarization rate, higher and higher portions of deposited Na are oxidized back, i.e. smaller and smaller amounts of Na are lost into bulk $NaCl$ by diffusion. It is probably due to the adsorption ability of Na to carbon sites. In other words, some kind of a surface NaC_x compound is stable. However, the rate of adsorption is lower than the rate of diffusion into bulk $NaCl$; that is why the stabilization of deposited Na is enhanced at lower rates of polarization. This enhanced stabilization is clearer from Fig.13, being the difference of Fig-s 11 and 10.

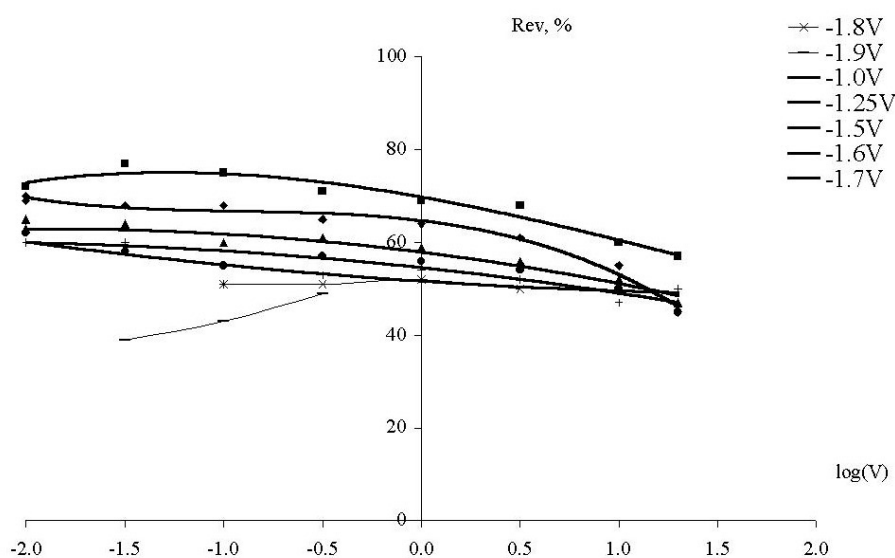


Fig. 11. Reversibility parameter Rev as a function of polarization rate (semi-logarithmic scale) at different break potentials (Reference electrode - Mo) measured on a GC electrode in pure $NaCl$ at $850\text{ }^{\circ}C$

iii. for the graphite working electrode the Rev values have approximately the same (somewhat larger) values at the largest rate of polarization of 20 V/s, compared to the GC working electrode. Then, at about 3 V/s, the Rev parameter has a maximum value. At this point the Rev parameter on the graphite electrode is significantly larger than on the GC electrode. In other words, the graphite surface has a higher stabilizing ability for Na atoms, compared to the GC surface. It is probably due to the higher roughness, i.e. higher specific surface area of the graphite compared to the GC, ensuring adsorption of the higher amount of Na atoms. However, with decreasing the polarization rate, the Rev parameter on the graphite electrode sharply decreases towards 0 %, in contrary to what

was observed for the glassy carbon electrode. This is obviously due to the diffusion of *Na* atoms into the graphite phase, and to the stabilization of *Na* atoms inside graphite by the formation of a stable intercalation compound. This feature is better seen from Fig.14, being the difference of Fig-s 12 and 11.

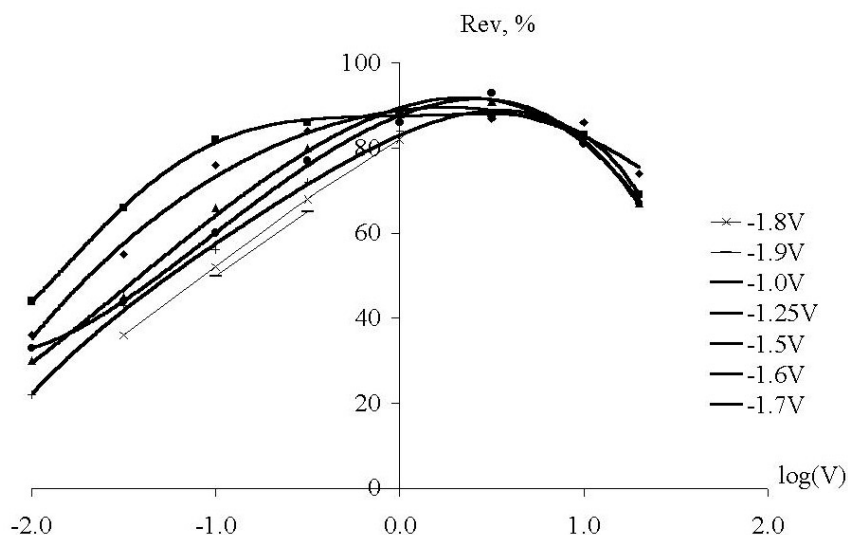


Fig. 12. Reversibility parameter *Rev* as a function of polarization rate (semi-logarithmic scale) at different break potentials (Reference electrode - *Mo*) measured on a graphite electrode in pure *NaCl* at 850°C.

Our statements about adsorption and intercalation are supported by the shape and characteristics of the voltammograms shown. In Fig. 1 through 9 a tendency to broadening of the anodic peak as well as its shifting towards more positive values of potential is observed as we move from the molybdenum to the glassy carbon and then further to the graphite electrode. Usually such behavior takes place when adsorption/compound formation is involved in the reduction process. So the shape and parameters of the voltammetric curves presented may be evidence that adsorption in the case of glassy carbon and adsorption/intercalation in the case of graphite electrode play an important role in the reduction process of sodium.

From the comparison of Fig-s 10-14, one can conclude that the rates of the three competitive processes can be presented in the following order:

- i. the fastest is the diffusion of *Na* into *NaCl*, probably due to the special electron-jump mechanism;
- ii. adsorption of *Na* on the carbon sites has an intermediate rate;
- iii. the slowest is the diffusion of sodium into graphite with the formation of the intercalation compound.

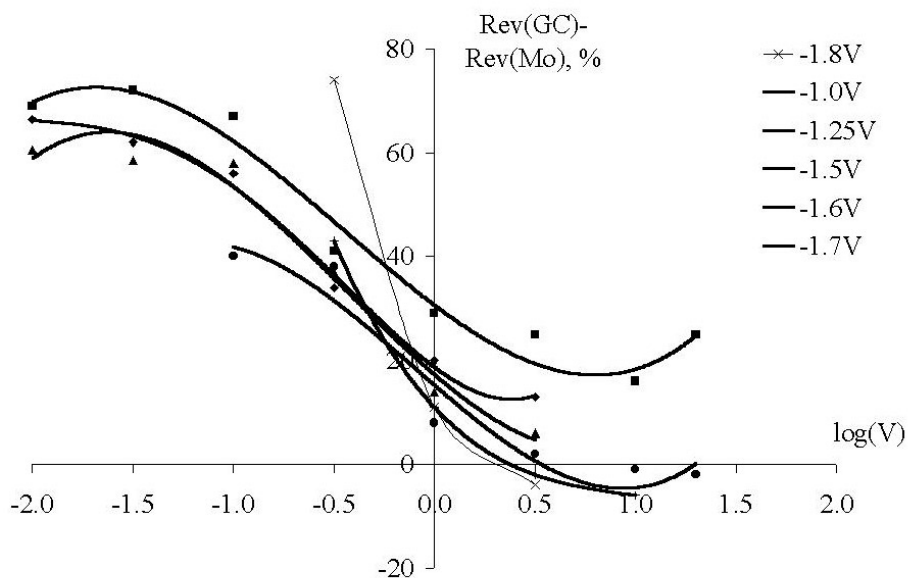


Fig. 13. The difference of reversibility parameters Rev between GC and Mo working electrodes (i.e. difference of Fig-s. 11 and 10).

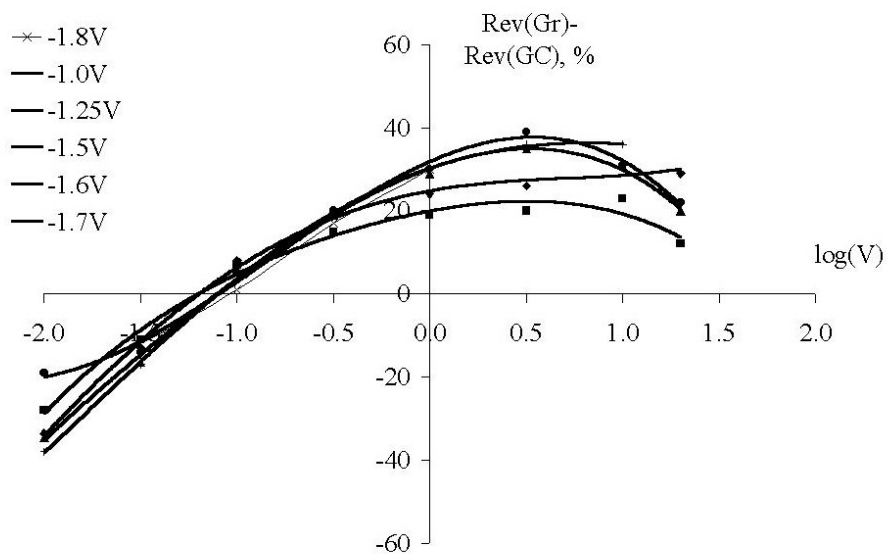


Fig. 14. The difference of reversibility parameters Rev between graphite (Gr) and GC working electrodes (i.e. difference of Fig-s. 12 and 11).

4. Conclusions

It has been shown that the process of sodium electroreduction on the three electrodes used is complicated by the dissolution of sodium in the melt in the whole range of polarization rates. The adsorption of sodium on glassy carbon and graphite plays an important role in the reduction of sodium at lower polarization rates (below 1 V/s). It makes the process reversibility higher compared to molybdenum. The intercalation of sodium into the graphite lattice decreases the overall reversibility of the process at low polarization rates (below 0.03 V/s).

In the future, we will attempt to develop a quantitative model of the above described processes, and thus to quantify the rates of diffusion and adsorption/desorption of *Na* including the rate of its intercalation into graphite. Also, we are going to perform a similar experimental program for the *LiCl*, *MgCl₂* and *CaCl₂* systems, and thus evaluate the difference in intercalating abilities of *Li*, *Na*, *Mg* and *Ca*.

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References:

1. S. Iijima, *Nature*, 354 (1991) 56.
2. W.K. Hsu, J.P. Hare, M. Terrones, H.W. Kroto, D.R.M. Walton, P.J.F. Harris, *Nature*, 377 (1995) 687.
3. W.K. Hsu, M. Terrones, J.P. Hare, H. Terrones, H.W. Kroto, D.R.M. Walton, *Chem. Phys. Lett.*, 262 (1996) 161.
4. G.Z. Chen, X. Fan, A. Luget, M.S.P. Shaffer, D.J. Fray, A.H. Windle, *J. Electroanal. Chem.*, 446 (1998) 1.
5. G.Z. Chen, I. Kinloch, M.S.P. Shaffer, D.J. Fray, A.H. Windle, in: *Advances in Molten Salts – From Structural Aspects to Waste Processing*, Edited by M. Gaune-Escard, Begell House, Inc., 1999, 97-107.
6. D.J. Fray, in: *Advances in Molten Salts – From Structural Aspects to Waste Processing*, Edited by M. Gaune-Escard, Begell House, Inc., 1999, 196-207.
7. G.Z. Chen, D.J. Fray, see this volume.
8. M.S. Yaghmaee, *Zs. Demeter*, see this volume.
9. G. Kaptay, I. Sytchev, M.S. Yaghmaee, A. Kovacs, E. Cserta, M. Ark, *Proc. 6th International Symposium on Molten Salt Chemistry and Technology*, Shanghai, China, 2001, p. 168.
10. Q. Xu, C. Schwandt, G.Z. Chen, D.J. Fray, *J. Electroanal. Chem.*, 530 (2002) 16.
11. G. Kaptay, J. Sytchev, J. Miklósi, P. Nagy, P. Póczik, K. Papp, E. Kálmán: *Progress in Molten Salt Chemistry*, Elsevier, vol. 1, 2000, p. 257.
12. M.V. Smirnov, V.V. Chebykin, L.A. Tsioukina, *Electrochimica Acta*, 26 (1981) 1275.