

Electrochemical Characterisation of a Nanoporous Carbon after Negative Polarisation by means of a Single Particle Microelectrode Technique

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Introduction

A single particle microelectrode technique with a micromanipulator [1] was applied for the characterisation of the electrochemical and mass transport properties of a high surface area nanoporous carbon, used as electrode material for double layer capacitor (DLC) [2]. Gas-porosimetry measurements have shown that the pores in the carbon are 8.2 ± 0.2 Å wide and extremely uniform in size [3]. The microelectrode technique, used in this work, has the advantage of reduced IR drop and the resistance due to external mass transport. The carbon material is obtained from silicon carbide, and suffers a thermal treatment, at approx. 1000 °C, with chlorine to produce silicon chloride and a solid skeleton carbon with very narrow pore size distribution according to the reaction: $\text{SiC (s)} + 2\text{Cl}_2 \text{(g)} \rightarrow \text{SiCl}_4 \text{(g)} + \text{C(s)}$. The solid carbon is, thereafter, purged with argon.

Experimental

The starting material was silicon carbide powder provided by NORTON AS. A nickel wire was used as a counter electrode and all the potential values were referred to the Hg|HgO reference electrode, immersed in 6M KOH. The electrochemical measurement system used for the experiments was Autolab II supplied by Eco Chemie BV. The particles were subjected to a pre-treatment in order to wet the inside of the particles, this consisted in boiling the particles in 6M KOH and, thereafter, exposing them to vacuum.

Results and discussion

The charge and discharge process for a particle, using a current of $\pm 3 \cdot 10^{-7}$ A, is illustrated in Fig. 1. The deviations from the ideal capacitive behaviour arisen at negative potentials, when processes such as hydrogen adsorption and evolution take place. The capacitance, C_s , estimated from the slope, $I/dE/dt$, for the charging process, increases for negative potentials larger than -0.5 V. At this potential the hydrogen adsorption starts in the nanopores. The reversibility and hydrogen uptake by oxygen functional groups has been investigated, since the amount of hydrogen adsorbed can be increased as the surface functionality of the carbon increases [4]. The increase in C_s , is, thus, explained as a pseudo-capacitance caused by the hydrogen adsorption on the pore wall and on the functional groups. In order to make a distinction between these two cases, an electrochemical oxidation (activation) was performed for several particles by cycling to 0.5V, and the potential was, after that, fixed at -0.85 V. Cyclic voltammetry showed, thereafter, a common anodic peak between 0 and 0.1V for oxidised and non-oxidised particles. Thus, hydrogen desorption seems to occur between 0 and 0.1 V. Hydrogen evolution takes place at approx. -1.4 V.

The voltammogram in Fig.2 shows that, after the introduction of oxygen groups, other peaks arise at 0, -0.12 and -0.4V. The transient current, observed at the reversal of the potential and shown in Fig.3, indicates that the mass transport becomes hindered after the electrochemical oxidation. However, after holding the potential at -0.85V an improvement in mass transport properties is achieved.

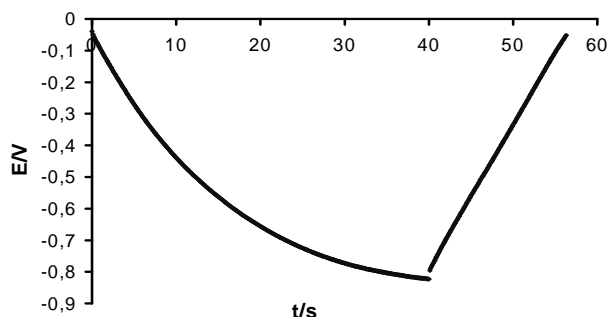


Figure 1 Galvanostatic charge & discharge, current $\pm 3 \cdot 10^{-7}$ A

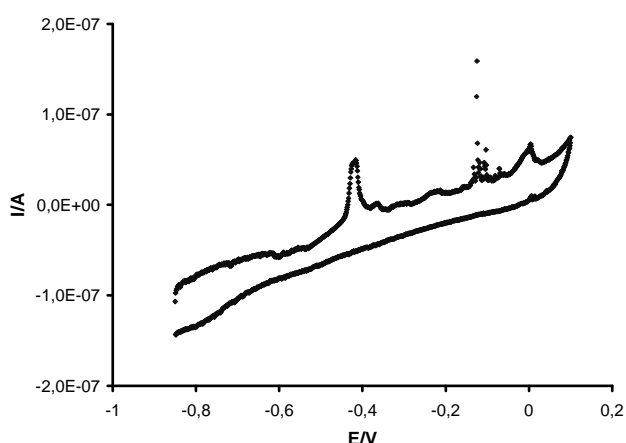


Figure 2 Cyclic voltammogram for oxidised particle performed after fixed potential 6 days at -0.85 V, scan rate 1mVs^{-1}

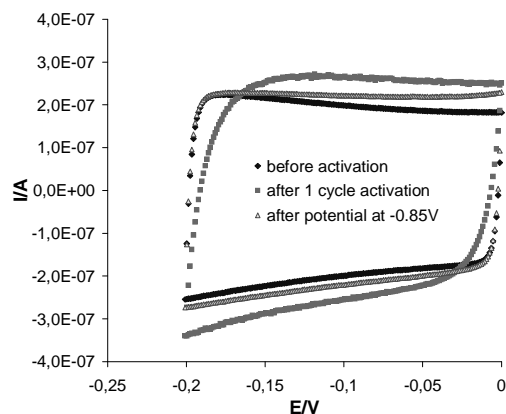


Figure 3 Cyclic voltammogram for the particle shown in Fig 2 at scan rate 10mVs and between potentials of pure capacitive behaviour

References

- [1] Bursell M and Björnbom P., J. Electrochem. Soc., 137 (1990) 363
- [2] US patent N5876787, 1999.
- [3] Zheng J., Ekström T.C., Gordeev S.K. and Jacob M., J. Mater. Chem., 10 (2000) 1039.
- [4] Miranda-Hernández M., Ayala J.A., Rincón M.E., J. Solid State Electrochem. 7 (2003) 264