

Characterization of electrodeposited carbon in molten carbonates and application to lithium batteries

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Carbon is commonly used in electrochemistry [1,2], either as an electrode material or as a host substance for intercalation compounds for example in lithium-ion batteries [3,4,5]. Several varieties of carbon from highly crystalline graphite to strongly disordered carbons depending to the synthesis conditions are available commercially. In order to obtain carbon coatings or carbon with special electrochemical properties, electrochemical route has been proposed. Cathodic reduction processes in carbonate melts have been studied because of their importance in molten fuel cell technology. In the present study, carbon deposits were obtained by electrochemical reduction of liquid ternary system lithium-sodium-potassium carbonate at 450°C on nickel and glassy carbon electrodes [6,7]. The influences of the deposit potential as well as the heating treatment after washing in HCl were studied. The electrochemical mechanism of carbon deposit was determined from the analysis with cyclic voltamograms, taking into account the influence of lithium ions present in the molten salt. The exploitation of these results coupled with thermodynamic data have shown that the electrochemical reduction gives rise not only to the formation of carbon but also to the formation of lithium oxide.

The structural characteristics of the carbon powders have been determined by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), transmission electron microscopy (TEM), surface and pore texture analysis (BET).

The presence of nearly-metallic and ionic lithium (Li_2O and/or LiOH) on the surface of the powder was revealed by the analysis of the C1s, Li1s, and O1s regions in XPS spectra. The X-ray diffraction patterns have shown the presence of a mixture of amorphous carbon and graphite. The crystallinity of the carbon deposit is enhanced with increasing negative values of the deposit potential.

TEM analyses have confirmed the presence of amorphous carbon and graphite. As illustrated Fig.1, the size of primary particles (around 5 μm) corresponds to the accumulation of nanoparticles [8]. This geometry implies very high surface specific area. This assumption was confirmed by BET measurements, which reveal specific surface areas between 450 and 850 m^2/g , depending on the applied potential value in molten carbonates.

The electrochemical insertion/deinsertion of lithium cations into the carbon powder was studied in 1 M LiClO_4

– EC:DEC (1:1) solution at room temperature. The electrodeposited carbon powders exhibit a mixed behavior: a first long step similar to that obtained with amorphous carbon, and a plateau at around 0.1V vs Li/Li^+ as in the case of lithium insertion into graphite. After five cycles, the reversible capacity becomes constant and reaches a value of about 490 mAh/g. This value is about 30 percent higher than the theoretical value obtained with pure graphite. The shape of the charge/discharge curves is characterized by an hysteresis of potential which depends on the potential used for the electrodeposition of the carbon powders in molten carbonates.

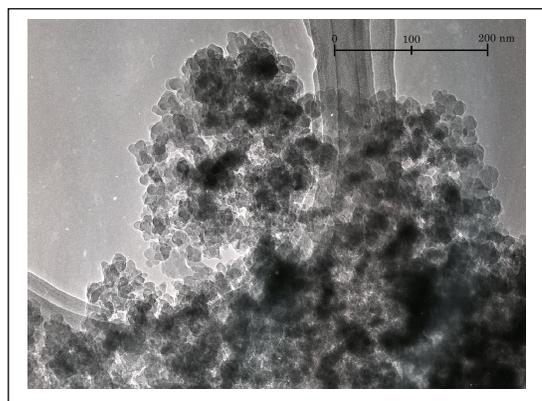


Figure 1. TEM image of amorphous carbon obtained by electrochemical reduction of liquid ternary system (Li-Na-K carbonates)

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