Electrodeposition of thin Silicon Films as Anode Materials for Lithium Ion Batteries

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High performance Li-ion batteries (LIB) are imperatively needed for electric vehicles and effective green energy storage devices. As a consequence, new electrode materials with higher energy density, enhanced rate capabilities and superior safety features are intensely studied [1].

Silicon has a very high theoretical specific capacity (4200 mAh/g) and is considered to be a next generation anode material. However, it suffers from problems arising from more than 300% volume changes during the alloying-dealloying process. This leads to electrode degradation and consequently to a rapid loss of capacity [2]. There are several studies directed toward overcoming this drawback, with a special emphasis on various techniques to nanostructure the silicon anodes. Besides nanostructured Si, thin amorphous films also effectively accommodate the large volume changes during Li insertion, which results in increased capacity retention and an improved cycle life.

Si nanowires, nanotubes and porous silicon showed improved electro-chemical performance, but most of them are obtained using expensive and/or complicated techniques. Alternatively, electrodeposition is a simple and inexpensive method for obtaining silicon films.

Ionic liquids attract much interest due to their exceptional properties (wide electro-chemical windows, low volatility and low flammability). These properties make them ideal electrolyte systems for both Si electrodeposition and its investigation as anode in high energy, rechargeable batteries [3]. Hence, the use of electrodeposited silicon anodes in combination with ionic liquid electrolytes may be very advantageous for the new generation of LIB with both high energy density and improved safety characteristics.

In our work, an electrodeposition method was employed to deposit silicon films on Cu substrates from the ionic liquid 1-butyl-1-methyl-pyrrolidinium bis (trifluoro-methyl) sulfonylimide ([BMP][TFSI]) containing 1M $SiCl_4$ [4]. The experiments were performed in a glovebox under inert atmosphere.

SEM and EDX investigations performed after the deposition confirmed that silicon had been electrodeposited on the copper electrode in the form of a compact layer with crystallite diameter of about 200 nm. The XRD measurements suggest that the deposited silicon is amorphous which is in agreement with literature reports [5].

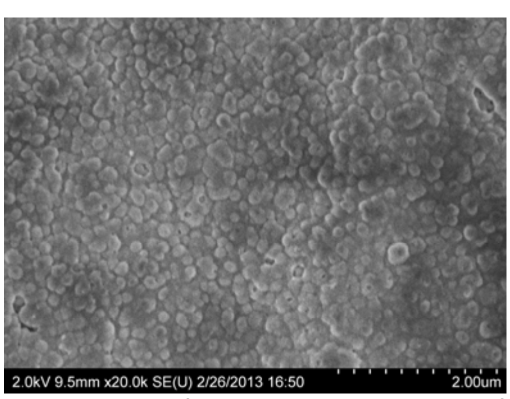

Fig.1 SEM image of the electrodeposited silicon film

The amount of electrodeposited silicon was estimated by QCM measurements and by integrating the current transients. The results analysis showed a current efficiency of almost 100% for the Si electrodeposition process.

The electrodeposited silicon films were subsequently tested as anodes for LIB by voltammetric and galvanostatic electrochemical cycling in the standard electrolyte 1M $LiPF_6$ ethylene carbonate dimethyl carbonate EC DMC (1:1) and in 1M LiTFSI in [BMP][TFSI].

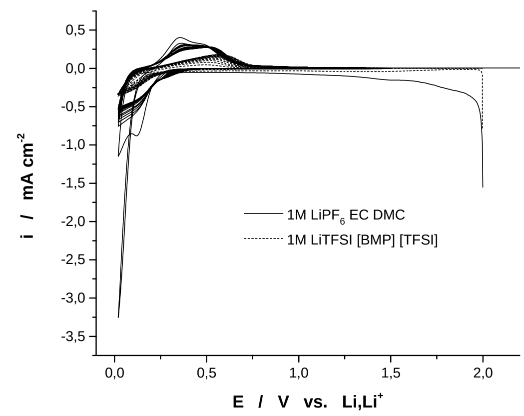

Fig. 2 Cyclic voltammograms of electrodeposited silicon

The results show stable cycling behavior for the thin silicon films both in ionic liquid and standard electrolyte. The capacity values are rather low (about 600mAh/g) when compared to the theoretical capacity of silicon and the reason for this is not clear so far. The capacity fade over 200 consecutive cycles was about 33%.

The silicon films obtained by electrodeposition show much promise as alternative anode materials in LIBs, but optimization of the deposition process is necessary and it is currently under investigation.

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