

STUDIES OF THE ELECTROCHEMICAL REACTION BETWEEN LITHIUM AND β -QUARTZ GeO_2

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Tin oxides are interesting candidates to substitute lithium and Li_xC_6 (lithiated graphite) as negative electrodes for lithium batteries, providing gravimetric and specific capacities as high as 600 mAh/g and 4.2kAh/L, during a few hundreds cycles [1,2]. Tin oxide reacts with lithium according to a mechanism with two steps [2,3]: first, the oxide decomposes yielding a tin particles/lithium oxide composite; next, the as formed tin particles electrochemically alloy with extra lithium. The first step is irreversible in the practical voltage range (0-1.0V) where tin oxide based cells are competitive versus the lithium based cells. However, the second step is reversible in the practical cycling range and accounts for the excellent performance above mentioned for tin oxide based cells.

Apart from tin, other group IV elements, M, can electrochemically and reversibly alloy with lithium in $\text{Li}/\text{LiCl}_x\text{KCl}/\text{M}$ cells at 400°C [4,5,6] or at room temperature in cells with non-aqueous solvent electrolyte [7,8]. For lithium batteries based on SiO [9] and PbO [10] or PbO_2 [11] materials, a mechanism of reaction analogous to the tin oxide cells was confirmed. First, the oxide dissociates and subsequently, the in situ formed metal (Si or Pb) further reacts with lithium yielding Li-Si or Li-Pb alloys. Therefore, and analogously to tin oxide, the silicon or lead oxides have been proposed as negative electrodes in lithium rechargeable batteries.

In spite of the above mentioned results, the electrochemical reaction between lithium and germanium oxides has not been studied. Some drawbacks for this study are the high cost of the element and more specifically for the β -quartz polymorph, its semiconductor behaviour, the 3D closed network without tunnels for lithium diffusion and the stability of the germanium-oxygen bond. In this presentation, preliminary results about the electrochemical reaction between lithium and β -quartz GeO_2 are reported. Factors in favour and against a mechanism analogous to tin oxide are analysed.

References

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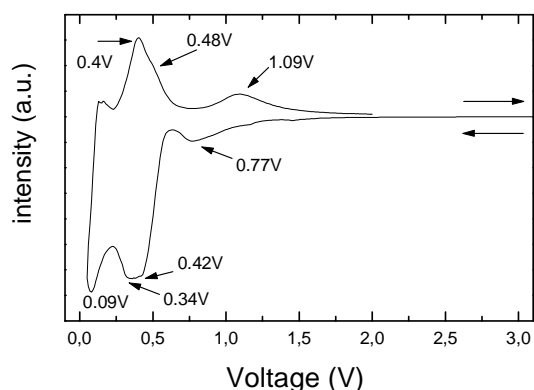


Figure 1. First potentiostatic cycle for one Li/LiPF_6 (EC, DEC)/ $\beta\text{-GeO}_2$ cell. (Voltage steps: 10 mV/10 min. Voltage range: 50 mV-2000 mV).

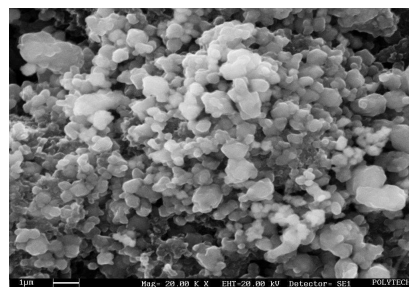


Figure 2. Scanning electron micrographs of a germanium oxide based electrode galvanostatically discharged at 50mV. Bar indicates 1 micron.