

## Electrochemical Activity of Tetragonal Tin in $\text{LiPF}_6$ -based Organic Electrolytes

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The polycrystalline  $\beta$ -Sn electrode shows high reactivity toward organic carbonate electrolytes during cathodic polarization at  $E < 2.5 \text{ V vs. Li/Li}^+$ . A large potential plateau that is usually observed at ca. 1.3 V during galvanostatic polarization [1] corresponds to the broad and intense cathodic current peak at similar potential in cyclic voltammograms [2]. Several authors have suggested that these irreversible cathodic processes originate from an electrocatalytic reduction of the electrolyte on various Sn crystal facets [1]. However, kinetic effects alone cannot explain large variations in electrolyte decomposition products and thickness, morphology, and stability of the surface layer. The goal of this study is to gain a fundamental understanding of the interfacial processes at Sn(100) and (001) single crystal electrodes in a 1M  $\text{LiPF}_6$  ethylene carbonate/diethyl carbonate (EC:DEC, 1:2, w:w) electrolyte.

*In situ* atomic force microscopy (AFM) and spectroscopic ellipsometry were used to study the mechanism of organic carbonate electrolytes decomposition. Interfacial phenomena were investigated at potentials above 0.8 V vs.  $\text{Li/Li}^+$ , i.e., where no Sn–Li alloying takes place and the single crystal character of the sample can be preserved throughout the experiment. Our previous studies [3] showed that the Sn(001) surface tends to form a protective surface layer of electrolyte reduction products during the first cathodic CV scan, which effectively inhibits further reduction of the electrolyte upon cycling. In contrast, the Sn(100) surface produces a thick, inhomogeneous and unstable surface layer. The observed significant difference of Sn reactivity toward the electrolyte as a function of Sn surface crystalline orientation suggests radically different reaction paths, reduction products, and properties of the surface film. These results were supported by reactivity of polycrystalline tin that was falling in between the two single crystal surfaces.

Our most recent measurements however shed new light on these results. We have identified that the native oxide layer present on tin exposed to air, and appreciable oxygen solubility in Sn have a major contribution to the electrochemical response of the Sn electrode. In this study we have prepared polycrystalline ultra-pure Sn samples through melting and purification of Sn inside a He-filled glove box. We have also polished the Sn single crystals under He atmosphere.

The two crystal surfaces still present different reactivity towards the electrolyte as depicted in the cyclic voltammograms, however they are vastly different from the reactivity observed for oxide-covered surfaces. Also the polycrystalline sample behaves differently.

SEM and EDX show different surface film composition on varying Sn surfaces confirming that the Sn surface structure has a strong influence on the catalytic activity in organic carbonate electrolytes.

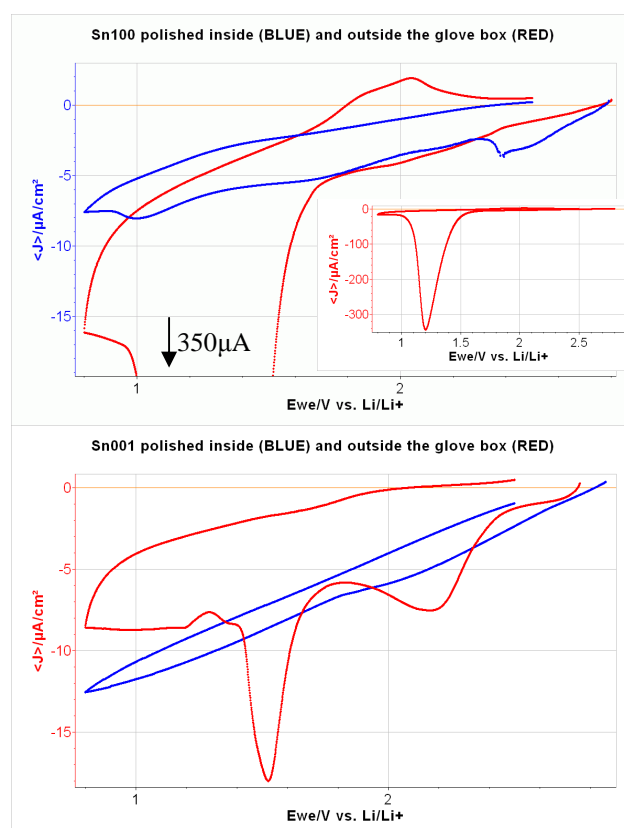


Figure 1. Cyclic voltammograms of Sn electrodes in 1M  $\text{LiPF}_6$ , EC:DEC (1:2, w:w) electrolyte at  $1 \text{ mV s}^{-1}$ ; (a) Sn(100), (b) Sn(001) polished inside and/or outside a He filled glove box ( $\text{O}_2$ ,  $\text{H}_2\text{O} < 0.1 \text{ ppm}$ ). Sn100 polished outside the glove box gives a current of  $-350 \mu\text{A}/\text{cm}^2$  (inset).

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### References

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