

Surface Modifications on the nm Scale: Single Crystal Li-ion Battery Anode Studied by In-situ X-ray Diffraction and Reflectivity

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We report first results of our experiments on the electrochemically-driven alloying and de-alloying of Au substrates with Li-ions from organic electrolytes studied by in-situ X-ray diffraction. We employed Synchrotron radiation at BL13XU under proposal number 2007A1963. Au(111) single crystals, 111-textured thin Au films and nanometer-sized Au particles on HOPG have been examined using a specially designed in-situ X-ray cell. Starting from single crystalline Au systems we could follow the structural degradation and pulverization under different electrochemical conditions. Reciprocal lattice space maps show the occurrence of powder-like intensity associated with different Li-Au alloy phases. The diffraction data from the bulk Au crystals is compared with the Au(111) thin films and the behavior of the Au nano-particles on HOPG.

The development of cost-effective, durable, and safe (mobile) energy systems is a key research challenge in the 21st century. Rechargeable (secondary) Li-Ion batteries, in particular, enabled the widespread use of mobile computers in the last decade due to their increased specific energy (capacity). The use of Li-ion batteries in Hybrid Electric Vehicles (HEV) has recently boosted research efforts. New ways have to be found to make a fast battery (high rate). Li-ion technology can achieve more than 2000 W/kg but safety is still low and the rate needs to be even further increased. Also a big problem is capacity fading.

Despite the importance of the electrode-electrolyte interface structure there are hardly interface-structure sensitive studies yet, but world-wide research focuses increasingly on the interface, which is very challenging! Fundamental (in-situ) knowledge of the Li-ion electrode-electrolyte interface is urgently needed.

X-ray diffraction offers a unique tool to study the structure of a buried electrode-electrolyte interface and of the interface-near region of the electrode in-situ with controlled potential, and is especially powerful when single crystal substrates are used.

We studied Au single crystals, thin Au films (150nm) on mica, and Au nano-particles (7nm) on HOPG and used battery-grade liquid organic electrolyte. For performing in-situ experiments at the solid-liquid battery-anode-electrolyte interface we used a high photon energy (~25 keV, for penetration of several mm of liquid without large absorption) and a high photon flux to obtain a signal from the surface structure.

We prepared the nm-scale Au film on HOPG by rf sputtering. AFM images of the films and X-ray data show the preferential 111-oriented growth of Au/HOPG and a mosaic width of ~3 degrees. A custom made in-situ X-ray diffraction cell was used. The sample is surrounded by an

inert gas atmosphere (Ar, He) to prevent electrolyte decomposition that occurs at potentials close to the very negative Li Nernst potential. Contact with oxygen or nitrogen has thus to be prevented.

Fig.1 shows a reciprocal space map around the Au(101) reflection (given in usual hexagonal surface coordinates). While the pristine Au sample shows only the Au (101) reflection and the intensity due to the surface truncation rod (CTR) shown as the dashed line, after the interaction with Li at a potential of 200mV vs Li powder-like features are clearly visible. Nevertheless, the preferred orientation of the new structures is clearly related to the original Au lattice. This is also shown in Fig. 2b, where the existence of peaks close to the Au peak

position indicates also such an preferred orientation in the perpendicular direction. The exact position of the small peaks along such a scan shows several possible orientations are possible with regard to the original host matrix, but clearly influenced by the original matrix. The large peak at the blue scan 3 in Figure 1b is due to the close-by Au (012) reflection [with a shift of 60 degrees in phi with respect to the Au(101)]. The new peaks, on the other side seem not to show the same fcc stacking as the host but show a six-fold symmetry (hcp or twins).

Very similar results have been obtained from the Au nano-particles on HOPG. Fig.1c shows specular scans after charging the anode with Li-ions. After some time the Au peak has vanished nearly completely, indicating the full transformation of the Au particles to Li-Au alloys. A small peak close to the original Au peak indicates the presence of a low-Li alloy (Up to 39% at. Li, keeping the crystal structure of Au). The main peak indicates a high Li-containing alloy and has been also observed with the Au crystal. An interesting detail is the fact that shortly after the start of the process the Au peak is already very small with the alloy peaks only slowly growing. Apparently a disordered regime is observed directly after the start of charging and before the crystalline, ordered phases are visible. This means that the Li alloying takes place homogeneously for all particles at the same time and that order is obtained only later.

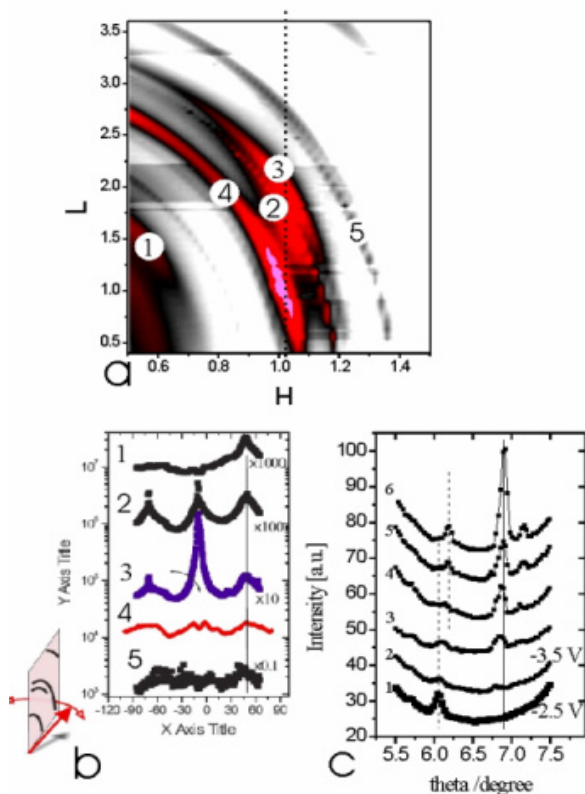


Fig.1 Some results of this proposal.