Electrolyte-electrode interface and Si deposition in ionic liquid

J. Komadina[ab], T. Akiyoshi[a], Y. Ishibashi[a], Y. Fukunaka[bcd], P. Pianetta[e], T. Homma[ab]

[a] Department of Applied Chemistry, Waseda University, Tokyo, Japan
[b] JST-CREST
[c] Japan Aerospace Exploration Agency (JAXA)
[d] Nanotechnology Research Center (NTRC), Waseda University, Tokyo, Japan
[e] Stanford Synchrotron Radiation Lightsource (SSRL) Menlo Park, CA

Several recent studies have demonstrated Si electroplating from nonaqueous systems such as ionic liquids[1,2]. Room temperature ionic liquids exhibit low volatility and can be treated to very low water impurity levels. The non-aqueous nature of ionic liquids allows for a large electrochemical window, often 4 or 5 V limited by irreversible breakdown of anions and cations, allowing for electrodeposition of elements such as Si and Li.

We have previously reported electrodeposition of Si from the ionic liquid trimethyl-n-hexylammonium bis(trifluoromethylsulfonyl)imide (TMHATFSI or $[N_{6111}][Tf_2N]$)[2], as well as the formation of Si nanodots[3] and nanopillars[4] on a gold substrate by nanoimprinting UV-curable resin (TR-21, Toyo Gosei Co) with a quartz mold[5]. Currently, crystalline and high-purity deposits of silicon from ionic liquid have not been demonstrated in our lab or reported in the literature.

Electrochemical quartz microbalance (EQCM) impedance analysis allows for *in situ* estimation of mass-charge ratio (m/z) and instantaneous measurement of solution viscosity in an electrochemical process. We have recently observed impure silicon electrodeposition with an apparent Si m/z suggestive of a 4-electron reduction of silicon[6,7]. This result is achieved by considering the mass of impurities observed with XPS/EDX, including significant ionic liquid in the deposits and partial oxidation to SiO_x or $Si(OH)_x$.

It has been suggested by others that molecular layering of ionic liquids and adsorption on the deposition frontier surface have a significant influence on the chemistry of electrodeposition in such electrolytes[8]. We are presently engaged in examining the impact on Si deposition of temperature, concentration of diluents, and electrode potential in TMHATFSI. To complement these studies, we are attempting to study the changes in ionic liquid – electrode interface structure by x-ray reflection measurements at the Stanford Synchrotron Radiation Lightsource.

This presentation will discuss the progress of our studies of the Si electrodeposition mechanism in light of our results at SSRL and the corresponding in-situ and ex-situ Si deposition measurements at Waseda University.

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