

Effect of Mass Transport on Si Electrodeposition in Aqueous Hydrazine

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An anomalous mass transport effect is observed for the processes of anodic dissolution and passivation of Si in aqueous hydrazine. Figure 1 compares the cyclic voltammograms obtained with a p-Si electrode in 10 M hydrazine, either not stirred (continuous line) or stirred (dashed line). Under conditions of faster mass transfer (i) a lower peak current is reached and (ii) passivation occurs at a lower potential, mostly as a consequence of the lower IR drop. Figure 2 shows the results of an experiment performed in a submerged impinging jet cell:¹ the mass transport rate (expressed by the Reynolds number Re) was modified in steps and the current density j followed vs. time, for a constant applied potential. Lower j values are obtained as Re increases. The effect of mass transport becomes stronger at higher potential and, in a restricted potential range, stirring may convert a state of active dissolution into a passive one.

Experiments performed under comparable conditions in NaOH solutions show a minor increase of current density on increasing the mass transfer, a phenomenon which may be largely attributed to more efficient removal of the hydrogen bubbles formed in the chemical etching process. In the case of aqueous hydrazine, the decrease of j on increasing mass transfer rate is more pronounced at lower temperatures, is observed both in the presence and in the absence of dissolved oxygen, and is markedly reduced when a significant concentration of NaOH is added to the hydrazine solution.

Data are interpreted by modifying a reaction mechanism previously proposed for Si dissolution in NaOH,² and consisting of four steps (besides a chemical etching process): (i) electrochemical oxidation of hydrogen terminated Si surface sites to monohydroxylated Si sites, (ii) electrochemical oxidation of mono- to dihydroxylated Si sites, (iii) chemical dissolution of monohydroxylated Si sites to a Si(II) species and (iv) chemical dissolution of dihydroxylated Si sites to a Si(IV) species. In the case of aqueous hydrazine, it is assumed that hydrazinium ions, produced in electrochemical oxidation steps similar to (i) and (ii), increase the rate of the chemical steps (iii) and (iv) leading to dissolution of Si species. In this frame, the effect of forced convection may be attributed to an enhanced removal of hydrazinium ions from the interface, decreasing the rate of these dissolution steps and of the overall electrodeposition process.

References

1. D.-T. Chin, C. H. Chang, *J. Electrochem. Soc.* **125**, 1461 (1978).
2. S. Cattarin and M.M. Musiani, *J. Phys. Chem. B* **103**, 3162 (1999).

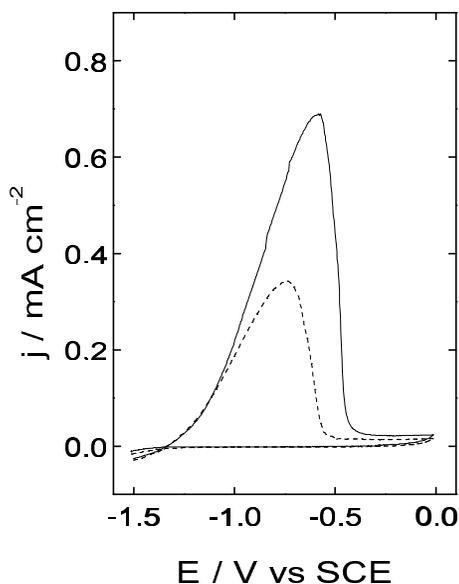


Figure 1. Cyclic voltammetry (5 mV s^{-1}) recorded at a p-Si electrode in 10 M N_2H_4 purged with N_2 , at $T = 50^\circ\text{C}$; solution is not stirred (continuous line) or stirred with a magnetic bar (dashed line).

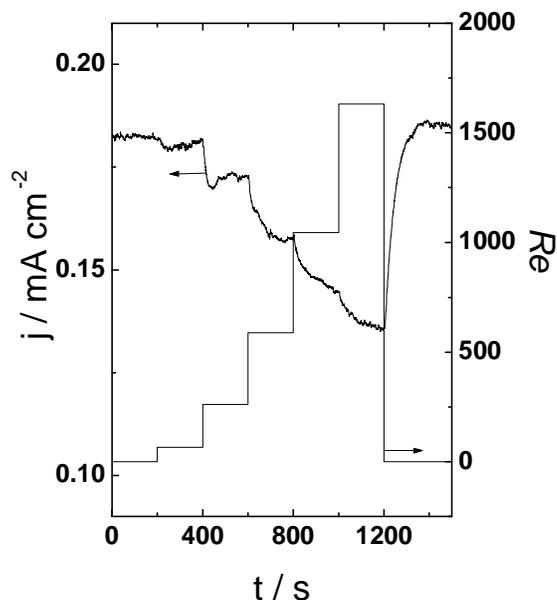


Figure 2. Effect of stirring on electrode current density in the SIJ cell at applied potential -0.85 V , $T=25^\circ\text{C}$. Pump rotation rate is varied stepwise and maintained for 200 s at each value of Re .