Electrochemical Processes in Neat Salt Electrolytes

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Although water (H_2O) is vital to the health of most living things, bulk water in electrolytes can interfere with electrochemical processing by reacting with an electrode, reactant or product. Recently ionic liquids and similar solid salt electrolytes have been synthesized that need no water, or any other solvents, for attaining conductivities that are as high, or even higher, than traditional aqueous electrolytes. Using salts as electrolytes also gives "greener" processing, since the salt electrolytes are not volatile.

The adverse effect of water during electrochemical processing is clearly illustrated during any attempt to electroplate a metal (M) whose metal-oxide (MO) has a highly exothermic heat of formation. Water interferes as a result of "local cell corrosion", which is summarized in reactions 1 to 3 below.

(Reaction 1) $M + H_2O \rightarrow MO + 2\ e^- + 2\ H^+$
(Reaction 2) $2\ e^- + 2\ H^+ \rightarrow H_2$
(Net Reaction 3) $M + H_2O \rightarrow MO + H_2$

The metal (M) and bulk water spontaneously react to form metal-oxide (MO) and protons (H^+) on one part of the metal surface (as shown in Reaction 1). At the same time, H^+ (from another bulk water molecule) is reduced on another part of the metal surface, forming hydrogen gas (H_2) (as shown in Reaction 2). The net result is the loss of metal and water and the formation of metal-oxide and hydrogen gas (as shown in the Net Reaction 3). Metals like aluminum and silicon can not be plated from their common ores (Al^{+3}, Si^{+4}, etc.) in aqueous solution, because the heats of formation of their metal-oxides are so highly exothermic that as soon as such a metal forms on a cathode, the metal reacts with water and reverts to its oxide (e.g., Al_2O_3, SiO_2, etc.). Furthermore, the metal oxides typically have high electrical resistivity and insulate the electrode and halt cell activity. Even "noble metals", like Pt, react with bulk water at electrode potentials greater than 0.9 volt versus the hydrogen electrode to form surface oxides, which lead to poor oxygen electrode performance of Pt catalyzed electrodes.

Bulk water activity and consequently metal oxide formation (shown in Reaction 1) that inhibits or prohibits cathode activity can be avoided by using a salt electrolyte. An overview the electrochemistry in low-water-activity salt electrolytes will be presented, with an emphasis on achieving more efficient fuel cells and the electrodeposition of semiconducting Si.