

Induced Codeposition of Mo and W from Aqueous Electrolytes

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Mo and W alloys are recognized for their outstanding corrosion, wear resistance and catalytic properties towards the generation of hydrogen. The electrochemical codeposition behavior of Mo or W with iron-group elements (*i.e.*, Ni, Co, Fe) exhibits induced codeposition, since they cannot be reduced alone, but only with iron group elements. Although Mo and W have been intensively investigated, their reaction mechanisms remain not well understood.

In work presented here, Mo induced codeposition with Ni was explored when the concentration of nickel ions in the electrolyte was much lower than molybdate. Their composition and deposit thickness were characterized by X-ray fluorescence. At this limit, the nickel species is expected to limit the reaction rate of molybdate reduction. Mo-rich alloys were obtained, setting a new record, with > 80 wt. % Mo content. Mo-rich MoNi deposits' morphology was examined by scanning electron microscopy. The MoNi alloys had a nodular morphology and contained micro-cracks, attributed to the large hydrogen evolution side reaction rate. Catalytic properties were investigated and exhibited Tafel behavior consistent with their hallmark feature as a catalyst for electrolytic hydrogen evolution. MoWNi alloys were also electrodeposited from aqueous electrolytes. The nickel preferentially induced the deposition of molybdenum over that of tungsten. The tungsten partial current density, hence reaction rate, was inhibited when deposition was compared to a molybdenum free electrolyte.

To probe the codeposition of the intermediate, preliminary work examined the affect of UV light on MoNi induced codeposition. Further investigation to consider UV excitation on NiMoW and NiW codeposition is proposed. The limits of MoNi induced codeposition will be further explored by varying electrodeposition bath's pH and ratio of Mo (VI) over Ni (II) to improve the current efficiency in an effort to reduce the amount of cracks in the deposit and to determine if there is an upper limit to the content of Mo in the deposit when codeposited with Ni. Since there has been an unusual observation of molybdenum inhibiting tungsten codeposition in the MoWNI electrodeposition system, future experiments will focus on a comparison of the metal reduction reaction rates when deposition is carried out with varying amounts of molybdate in the electrolyte. These studies will contribute to the understanding of the induced codeposition phenomenon and map deposition conditions for Mo and W alloys for a variety of technologically interesting applications.