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 the 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. 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. A mechanism to describe this observation was raised for both Mo and W induced codeposition.

To probe the intermediate of induced codeposition, intensity modulated photocurrent spectroscopy (IMPS) was performed to assess the intermediate species occurring during induced codeposition of NiW. Results support the presence of adsorbed intermediates that form during electrodeposition that is photoactive. It was also observed that the frequency where the imaginary component of the ratio of photocurrent over light flux is the largest, f_{max}, and the size of the semicircle generated by IMPS, depended on applied potentials.

Pulse electrodeposition was also conducted to investigate the induced codeposition. It was observed that an increase of duty cycle can lead a decrease of Mo content and an increase of W content in deposit, but no significant change in Ni, attributed to differences in adsorbed molybdenum and tungsten intermediate species. Additionally pulse electrodeposition helps to tune the density of cracks in the deposits by varying the duty cycle.

In this work, the composition range of electrodeposited NiMo from aqueous solution was expanded to a new limit, 80 wt.%. Also, a new mechanism of Mo and W induced codeposition was suggested, where adsorbed intermediates was identified as the key species that induces molybdate and tungstate ion reduction. For the first time, IMPS was applied to an electrodeposition system, and used to verify adsorbed intermediates during NiW codeposition.