Photochemical Route for the Preparation of Complex Amorphous Water Oxidation Catalysts

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Recent years have seen a significant effort directed toward the development of amorphous metal oxide films as electrocatalysts that mediate the oxygen evolving reaction (OER).[1-5] The fabrication methods available for such catalysts are limited, however, and rely almost exclusively on electrodeposition or techniques requiring specialized equipment that often lack versatility and simplicity. Consequently, a small number of compositions have been reported for amorphous metal oxides relative to crystalline metal oxides. We therefore sought to expand the catalogue of amorphous metal oxide catalysts available through the introduction of a simple, rapid, versatile and inexpensive fabrication technique. In this vein, a series of films prepared by photochemical metal-organic decomposition (PMOD)[6] were examined in the context of OER catalysis. This process relies on the photochemical decomposition of appropriately chosen metal complexes to produce amorphous metal oxide films on electrode surfaces, and can be employed to prepare complex films containing multiple metallic elements. Initial results, where deposited films were analyzed by X-ray techniques, highlight acute control of the compositions of the resulting amorphous metal oxide films.[7] Indeed, the film compositions were shown to be directly proportional to the relative concentrations of metal complexes in precursor solutions. This outcome represents a significant advantage compared to the commonly employed electrodeposition techniques, where modification of the procedure is required to achieve deposition of oxides of the various metallic elements,[2,4] and the voltage protocol employed can have profound affects on film compositions.[4,8] Furthermore, heating the films to appropriate temperatures was shown to convert the as-deposited amorphous films to their more commonly observed crystalline forms, thereby enabling the rapid comparisons.

A variety of films have been prepared by PMOD and their electrocatalytic properties towards OER have been examined.[7] The amorphous films prepared by PMOD were shown to exhibit different properties than their crystalline counterparts. For example, the amorphous metal oxides consistently outperformed their crystalline counterparts in catalyzing OER, with improvements in both catalytic onset and measured Tafel slopes.

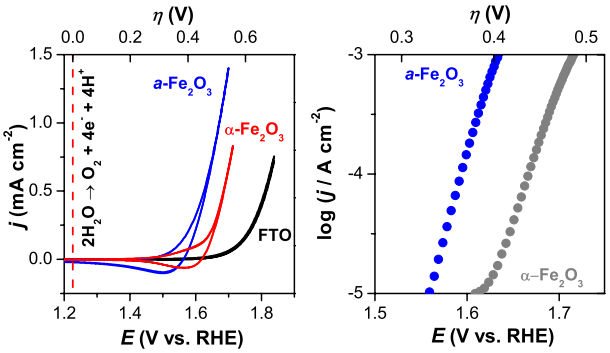

Figure: Electrocatalytic water oxidation by amorphous iron oxide (a-Fe_2O_3) prepared by photochemical route, hematite (α-Fe_2O_3) and the blank FTO support.

The introduction of PMOD for the preparation of amorphous metal oxide electrocatalysts is expected to greatly broaden the applicability and ease of study of amorphous OER catalysts. The technique is directly applicable to the majority of metallic elements in the periodic table, and when coupled with the precise control of elemental composition, enables access to a staggering number of amorphous materials for electrochemical study.

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