審査の結果の要旨

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Nickel-cerium oxide catalysts for water electrolysis

PhD thesis defended by Jun YU

For renewable energy sources to become practical as baseload sources, energy conversion technologies for storing energy must be developed. The oxygen evolution reaction (OER) in water splitting is a critical reaction for many such technologies. The discovery of a high-efficiency OER catalyst is the key to bringing a high-capacity energy storage technology one step closer to realization. Particularly non-noble metal catalysts with high activity and stability made from earth-abundant materials that can be fabricated on a three dimensional substrate (e.g. hierarchical porous substrates) with a low-cost technique are in high demand. Recently Jaramillo’s group reported a new non-noble metal catalyst based on $NiCeO_x$ (Nature Energy 1, 16053, 2016). When the catalyst layer is deposited on an Au layer, outstanding performance for efficiency is reported with a 271 mV overpotential at 10 mA/cm^2. The amount of cerium is found to control the efficiency of this catalyst with the highest efficiency achieved by adding a relatively small relative amount of cerium (5:95 Ce:Ni). The two-hour stability test conducted on the catalyst layer reveals an increase of the overpotential from 290 mV to 310 mV, thus suggesting some stability issue for this new material.

Jun demonstrates the synthesis of amorphous $NiCeO_x$ (50:50 Ce:Ni) on a Ni foam substrate through a simple two-step dip-coating/annealing process and reports stable operation of this catalyst layer for 100 hours. The thesis manuscript consists of four Chapters.

Chapter One reviews the major catalysts for use in OER and the techniques used to characterize their performance. Cerium based catalysts are introduced and the role of defects in these materials is reviewed. Characterization of defects for Ce-based materials is also reviewed. In Chapter Two, the effect of Ni atomic concentration on the properties of $NiCeO_x$ formed on a nickel foam substrate is investigated. Here, the Ni atomic concentration is controlled by the wet chemistry process (*i.e.*, concentration of Ni ions in the salt solution) and atomic thermal diffusion from the Ni foam is prevented by applying a prior thermal oxidation treatment of the nickel foam resulting in the formation of a NiO_x barrier layer. The Ni foam offers a large surface for chemical reaction and will be used in the synthesis of the final catalyst layer (Chapter Three) by thermal diffusion of Ni into the layer deposited by dip coating of a Ce salt solution. It is found that a concentration of Ce from 25 to 50 at% gives an amorphous layer with high catalytic activity as evidenced from low mass-transfer resistances, low Tafel slopes and large electrochemical active surface areas. This range of Ce concentration is also found to help the catalyst to offer stable electrolysis operation for 100 hours. The microstructural analysis (defects observed by Raman and Ce valence states observed by XPS) points to the formation of a large amount of oxygen vacancies that should promote water electrolysis activity. Thus, the effects of the cerium content on the catalyst microstructure suggests that the high activity of this catalyst layer is the result of the large number of defects in the amorphous $NiCeO_x$. The strong electronic interactions between nickel and cerium oxide result in these defects. Also, the large relative concentration of cerium (50:50 Ce:Ni) is thought to stabilize the catalyst layer. It is noted that significant improvement over Jaramillo’s group report (Nature Energy 1, 16053, 2016) has been achieved by eliminating the need for the Au layer to obtain a low overpotential and a stable operation over 100 hours. In Chapter Three, deposition of a cerium salt solution on the nickel foam and its subsequent annealing in air result in the formation of a $NiCeO_x$ layer on top of the nickel foam through thermally induced diffusion of nickel atoms from the nickel foam substrate into the top layer. Here, the number of dip-coating cycles is optimized to achieve the lowest overpotential for a fixed current of 10 mA/cm^2. This process in which nickel salt is not used enables for simple and efficient deposition of the catalytic layer on the nickel foam and also results in a good adhesion of the catalytic layer on the nickel foam due to the thermal diffusion. The catalytic behavior of the layers obtained by thermal diffusion is similar to that of the layer obtained by mixing Ce and Ni salt precursors as reported in Chapter Two. In Chapter Four, cross-sectional transmission electron microscopy is used to confirm that Ni and Ce are mixed uniformly in the catalyst layer with approximately the same ratio (50:50 Ce:Ni). The catalyst layer obtained by thermal diffusion exhibits a low overpotential of 295 mV at 10 mA/cm^2 and a stability of over 100 hours. The conclusions of the manuscript are given in Chapter Five.

In summary, a technique amenable to large scale production of a non-noble metal catalyst is presented, and the activity and stability of the synthesized catalyst layer are among the best for metal-oxide based catalysts, but still fail to surpass the top data reported by Sargent’s group on a cobalt based catalyst (Science 2016, 352, 333). Additionally, the activity of the $NiCeO_x$ catalyst for hydrogen evolution is superior to that of reported cerium-based catalysts including Pt-Ce, and so $NiCeO_x$ is the first reported cerium based bifunctional catalyst which can be used for overall water splitting.

よって本論文は博士（工学）の学位請求論文として合格と認められる。