論文の内容の要旨
Abstract

論文題目　Nickel-cerium oxide catalysts for water electrolysis
（水の電気分解におけるニッケル－セリウム酸化物触媒）

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For society to adapt to the growing demand for clean energy, renewable energy sources must be utilized to a greater degree. Unfortunately, the vast majority of renewable energy sources, such as wind and solar energy source, can only produce energy intermittently. For these renewable energy sources to replace conventional fossil fuel energy sources, energy storage technologies must be developed. A wide variety of energy conversion devices, including hydrogen fuel-cells, metal-air batteries and photoelectrochemical cells, have been explored to convert electrical or solar energy to chemical energy in order to store the energy produced by renewable energy sources. In all of these devices, the oxygen evolution reaction (OER) is a critical reaction. Because the OER is a four-electron reaction, a large overpotential is needed to overcome the large activation barrier and to drive the electrochemical reaction. Finding a suitable OER catalyst with a high efficiency, low overpotential, low-cost and long-term stability is key to enabling widespread adoption of renewable energy sources.

The best OER catalysts reported so far have generally been iridium or ruthenium-based oxides. The scarcity of both iridium and ruthenium, however, significantly limits the widespread use of these catalysts. First-row transition metals such as Ni- and Co-based oxides, have recently been studied as low-cost alternatives to iridium and ruthenium-based oxide catalysts. However, the OER activities of these catalysts need be further improved compared with the precious metal catalysts, and the stability is not high enough for industry application. Defects in catalysts can enhance the OER performance of the catalysts by altering the local electron density distribution and providing catalytically active sites. Ceria is an example of a non-stoichiometric catalyst material and Ce-based catalysts have exhibited higher catalytic activity for thermal catalytic reactions when defects are introduced into them. However, whether or not defects in ceria and ceria based catalysts can enhance the catalytic activity in low temperature reactions, such as water electrolysis, has yet to be discerned.

In this dissertation, a series of $Ni_yCe_{100-y}O_x$ ($Ni_{95}Ce_5O_x$, $Ni_{90}Ce_{10}O_x$, $Ni_{75}Ce_{25}O_x$, $Ni_{50}Ce_{50}O_x$, $Ni_{25}Ce_{75}O_x$ and $Ni_{10}Ce_{90}O_x$) with different Ni/Ce ratio are synthesized on NF (Nickel Foam)/NiO substrate with simple dip-coating and annealing methods. The surface NiO obtained from the oxidation of NF can prohibit the diffusion of Ni atoms to the deposited $Ni_yCe_{100-y}O_x$ so that the Ni/Ce ratio will be remained. Oxygen vacancy defects are formed successfully in all the NF/NiO/$Ni_yCe_{100-y}O_x$ (simply referred to $Ni_yCe_{100-y}O_x$) catalysts. The concentration of oxygen vacancy defects for $Ni_{75}Ce_{25}O_x$ and $Ni_{50}Ce_{50}O_x$ catalysts are larger than other $Ni_yCe_{100-y}O_x$ catalysts. The overpotential for the $Ni_{75}Ce_{25}O_x$ and $Ni_{50}Ce_{50}O_x$ catalysts are 338 mV and 341 mV to obtain a current density of 10 mA/cm^2, which are lower than other $Ni_yCe_{100-y}O_x$ catalysts. The better oxygen evolution activities of the $Ni_{75}Ce_{25}O_x$ and $Ni_{50}Ce_{50}O_x$ catalysts are because of their similar larger electrochemically active surface areas, lower Tafel slopes and lower charge-transfer resistances. Additionally, the $Ni_yCe_{100-y}O_x$ catalyst with high Ce content ($Ni_{75}Ce_{25}O_x$) is more stable than the $Ni_yCe_{100-y}O_x$ catalyst with low Ce content ($Ni_{95}Ce_5O_x$) during long-term water electrolysis with a fixed current density of 10 mA/cm^2.

For industry application, NF is used directly as the substrate instead of NF/NiO in order to simplify the synthesis process and reduce the material costs. A series of $NiCeO_x$ with different dip-coating times ($NiCeO_x$-Y) are synthesized directly on commercially available nickel foam (NF) using a simple, low-cost, environmentally friendly and reproducible synthesis method that consists of first dip-coating the NF in a cerium pre-cursor and then annealing the sample at 400 ° C. With the dip-coating times increasing from 1 to 20, the concentration of formed oxygen vacancy defects and the OER performance increase firstly and then decrease for $NiCeO_x$-Y catalysts. The $NiCeO_x$-15 catalyst has the largest concentration of oxygen vacancies and shows the best OER performance with the lowest overpotential of 295 mV for 10 mA/cm^2, and the applied potential remains constant for over 100 h for the fixed current density of 10 mA/cm^2. For the $NiCeO_x$ (simply referred to $NiCeO_x$-15) catalyst, Ni atoms from the nickel foam substrate transfer to the top layer and mix with deposited Ce uniformly to form an amorphous $NiCeO_x$ layer through thermal diffusion. The strong electronic interactions between nickel and cerium oxide induce the formation of oxygen vacancy defects in $NiCeO_x$. The large number of oxygen vacancy defects supply an abundance of active OER sites, resulting in the large electrochemically active surface area of the $NiCeO_x$ (ca. 34 times that of NF) catalyst. The oxygen vacancy defects in the $NiCeO_x$ catalyst also promote the mobility of lattice oxygen and enhance the ionic conductivity, resulting in the low mass-transfer resistance These bring in the high OER performance of the $NiCeO_x$ catalyst. In addition, the HER (hydrogen evolution reaction) activity of the $NiCeO_x$ catalyst is the best among the reported Ce-containing catalysts, including Pt-Ce. The stable performance of the $NiCeO_x$ catalyst in a two-electrode configuration suggests it is a good candidate as a bifunctional catalyst for the overall water splitting.

In summary, a defect-rich $NiCeO_x$ layer is directly synthesized on nickel foam through a simple two-step dip-coating/annealing method. The $NiCeO_x$ catalyst, with the low overpotential of 295 mV for 10 mA/cm^2 and the stability of over 100 hours, is one of the best OER catalysts ever reported, even outperforming the noble metal catalysts. The excellent performance and low-cost, environmentally friendly and reproducible synthesis method of $NiCeO_x$ catalyst make it suitable for industry application. In addition, the stable performance of the $NiCeO_x$ catalyst in a two-electrode configuration suggests it is a good candidate as a bifunctional catalyst for the overall water splitting. This work might open a new avenue for developing Ce-based OER catalysts with high efficiency and stable performance by introducing defects. Nickel foam can be used directly as the source of nickel for the synthesis of Ni-based catalysts through the thermal diffusion of Ni atoms.