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Synthesis and Characterization of $Co_xTi_yO_z$ as a Catalyst for the Oxygen Evolution Reaction

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Photoelectrochemical water splitting can be used to store solar energy in the form of hydrogen. However, the efficiency of the overall water splitting reaction is severely limited by the high overpotential costs required for the oxygen evolution half reaction. Furthermore, there exists a need for a nonprecious metal catalyst to drive the oxygen evolution reaction (OER) at low overpotentials to make the process more economical as well as more efficient.

As an alternative to the best known precious metal OER catalysts like RuO_2 and IrO_2, previous work has focused on manganese oxide and cobalt oxide catalysts.[1-3] We have identified amorphous $Co_xTi_yO_z$ as a novel, active, nonprecious metal catalyst for OER. Using a simple and scalable sol gel synthesis, thin films (50 nm – 200 nm) of $Co_xTi_yO_z$ can be deposited on a number of different substrates. This work begins by characterizing the structure and morphology of this material and studying the effect of varying the heat treatment temperature and elemental ratio of Co:Ti on catalytic activity and material stability. Furthermore, we characterize the effect of preparation route on the oxidation state of cobalt using *ex situ* L-edge x-ray absorption spectroscopy (XAS). We also investigate the effect of catalytic testing on cobalt oxidation state of the surface layer.

We have verified that crystalline $CoTiO_3$ is formed at calcination temperatures 550°C and above, however the lower temperature calcinations which result in an amorphous $CoTiO_x$ material produce better catalysts for the OER. A calcination temperature of 150°C produces a catalyst with a relatively low overpotential (~440 mV) to reach 10 mA/cm^2 and loses 24% of its initial activity over 15 hours of continuous testing. *Ex situ* XAS reveals that cobalt is in a mixed $2^+/3^+$ state when in the active form. This activity was further improved by varying the ratio of Co:Ti in the material. Increased amounts of cobalt resulted in improved catalytic activity with respect to the 1:1 case ($CoTiO_x$). Additionally, it was found that the red-ox potential of cobalt was shifted towards lower potentials by increasing the amount of cobalt in the material. *Ex situ* XAS again found that the more active catalysts had cobalt in a mixed $2^+/3^+$ oxidation state whereas the less active catalysts had cobalt in mostly a 2^+ state.

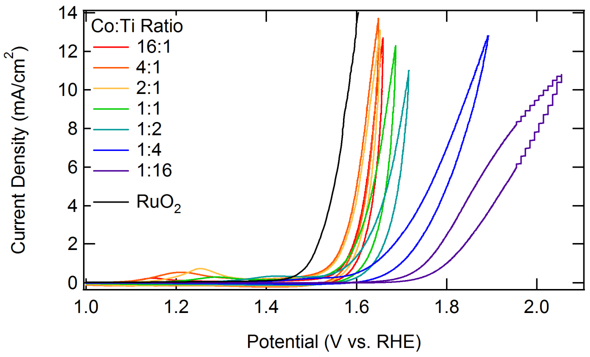

Figure 1. Catalytic activity of $Co_xTi_yO_z$ catalysts prepared with varying ratios of Co:Ti.

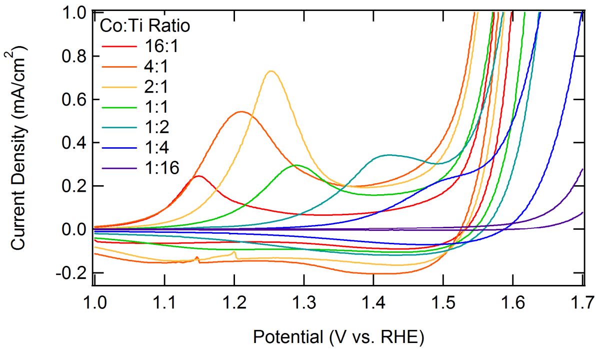

Figure 2. Shifted oxidation peak potential with respect to Co:Ti ratio of $Co_xTi_yO_z$ catalysts.

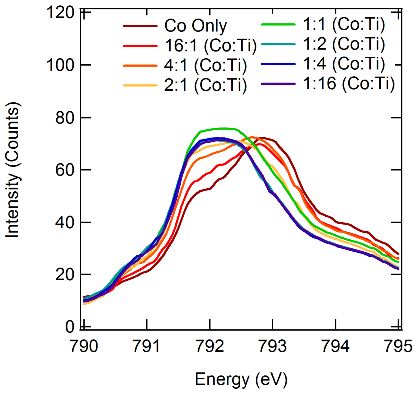

Figure 3. Ex situ XAS study of $Co_xTi_yO_z$ catalysts to determine change in oxidation state with respect to Co:Ti ratio.

References

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