

Copper Delafossite Anode for Water Electrolysis

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Electrochemical water splitting has been refocused in the recent years as a key process in hydrogen production from renewable energy. One of the most important issues for electrochemical water splitting is the development of an effective and inexpensive catalyst for the oxygen evolution reaction (OER).

A large number of researches have been conducted for the OER catalysts, especially oxides. We pay attention to delafossite oxides, which has been widely studied for the application to electronic devices as a transparent conductive film and a thermoelectric material. Precious metal delafossites were reported as good OER catalysts [1], but there has never been examined on delafossites consisted of non-precious metals like copper as the OER catalyst.

Recently it has been suggested that the anti-bonding e_g orbital occupancy of the surface transition metal cation of perovskite oxides has a strong correlation with the ORR and OER catalytic activities [2, 3]. In this study, we calculated the e_g orbital occupancy at the B site of copper delafossite oxides (ABO_2 ; A=Cu) to estimate their catalytic activity, and then confirm OER activity electrochemically.

All calculations in this work were carried out by using density-functional theory (DFT) as implemented in the STATE code, which has been successfully applied to metal surfaces and electrochemical interfaces [4]. Figure 1 shows that e_g occupancy of Cu delafossites from bulk DFT calculation. It has been reported that the OER catalytic activity becomes higher as the e_g occupancy is close to 1.0 [2]. According to this hypothesis, it is expected that the $CuRhO_2$ has highest OER activity among Cu delafossites in this work.

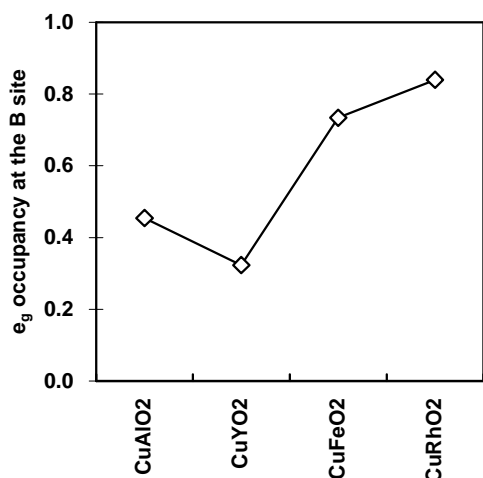


Figure 1 The bulk DFT calculation results of e_g orbital electron occupancy at the B site of Cu delafossites.

Then, we synthesized the Cu delafossites described in Figure 1, and evaluate the characteristics of their OER activities.

The samples of Cu delafossite were prepared by a conventional solid-state reaction. Stoichiometric monoxide precursors were mixed in agate mortar. The mixture were pressed in the form of a pellet and calcined at around 1050 °C for 12 h. It was confirmed from SEM and XRD measurement that synthesized compounds were polycrystalline particles of Cu delafossite with high crystallinity.

Particles of the Cu delafossite were deposited on a HPG carbon substrate and used as working electrodes (WE). A platinum plate and reversible hydrogen electrode (RHE) were used as the counter and reference electrodes, respectively. Current densities were calculated by using the geometrical surface area of the WE (0.283 cm²). Electrolyte was 1.0 M KOH aqueous solution (pH=14) and O₂ was bubbled during the measurement.

Figure 2 shows the curves of current density (j) vs. potential (U) for synthesized delafossites and Co_3O_4 , obtained by the RDE measurement. It was found that $CuRhO_2$ shows the significantly high current density among the delafossites obtained in this work. The onset potential of $CuRhO_2$ was almost the same as Co_3O_4 , which is known to have the highest OER activity among non-precious metal oxides. Furthermore, the j - U curve of $CuRhO_2$ did not change after 1000 cycles of measurements.

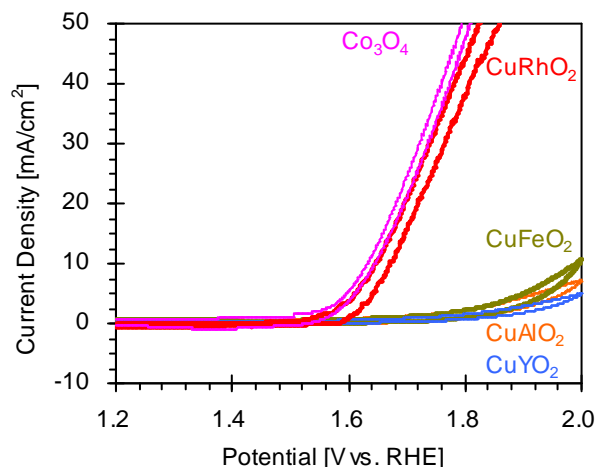


Figure 2 j vs. U curves for various catalysts in 1 M KOH at 50 mV/s scan rate at 2000 rpm.

We summarize that e_g occupancy obtained by bulk DFT calculation could predict OER catalytic activities of Cu delafossites, and $CuRhO_2$ found to have high catalytic OER activity and high stability in strong basic solution.

References

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