

Study on Synthesis of High Entropy Oxides for Enhanced Electrocatalytic Water Splitting

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論 文 名	Study on Synthesis of High Entropy Oxides for Enhanced Electrocatalytic Water Splitting (水の電気分解触媒としての高エントロピー酸化物の合成に関する研究)			
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論 文 審 査 の 結 果 の 要 旨

The growing demand for sustainable energy solutions has highlighted hydrogen as a promising clean energy carrier, with water electrolysis recognized as a viable method for green hydrogen production. However, the oxygen evolution reaction (OER) remains a major challenge due to its sluggish kinetics and reliance on scarce and expensive noble metal catalysts. This dissertation focuses on the development of high-entropy spinel oxides (HESOs) as efficient and earth-abundant electrocatalysts for OER in alkaline media. HESO is a complex oxide material with spinel structure containing five or more different cations which is promising for the application in electrocatalysis due to the synergistic effects. A key aspect of this study is the use of the molten salt synthesis (MSS) method, a green, cost-effective, and versatile approach for fabricating nanomaterials. MSS offers two notable advantages over conventional synthesis techniques: it significantly reduces the product formation temperature and enables the formation of uniform particles. The molten salt medium functions as an ionic liquid, where its strong polarizing nature facilitates the dissolution of various transition metal oxides. This property allows precise control over the composition of the resulting high-entropy oxide products.

The main findings obtained in this dissertation are as follows.

1. Equimolar ($(\text{Ni}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.2}\text{Zn}_{0.2})_3\text{O}_4$) and non-equimolar (CoMn-rich and NiFe-rich) HESO nanoparticles were successfully synthesized using MSS by precisely controlling the elemental ratios in the precursor mixture. The resulting nanoparticles exhibit a spinel crystal structure. Ex situ temperature-dependent X-ray diffraction analysis revealed that the major phase transformation occurs between 650 °C and 700 °C, coinciding with the melting point of the NaCl–KCl eutectic. The synthesized nanoparticles show high crystallinity and phase purity, with Fe, Ni, Co, Mn, and Zn elements uniformly distributed throughout the material. The scanning electron microscope-energy dispersive x-ray spectroscopy analysis reveals that the atomic ratios of the samples closely match those of the incorporated precursors.
2. The OER performance of both equimolar and non-equimolar HESO samples was evaluated, with the CoMn-rich composition demonstrating the best activity. It exhibited a lower

overpotential, faster reaction kinetics, and superior charge transfer capability. X-ray photoelectron spectroscopy (XPS) analysis revealed that the CoMn-rich HESO contains a higher proportion of high-valence species, which likely contributes to the enhanced OER performance. Additionally, this sample showed a greater adsorption capacity for oxygen-containing intermediates. These findings indicate that, although the HESOs share the same constituent elements, tuning their elemental ratios can significantly influence their physicochemical properties and thereby optimize their electrocatalytic performance.

3. A RuO₂/HESO heterostructure was further developed using the MSS method. XPS analysis confirmed strong electronic interactions at the RuO₂/HESO interface, resulting in an optimized electronic structure and an increased concentration of surface lattice oxygen species. These factors are critical for enhancing intermediate adsorption and overall OER activity. As a result, the heterostructure catalyst exhibits significantly improved OER performance, characterized by a reduced overpotential, a smaller Tafel slope, and decreased charge transfer resistance.

In summary, this dissertation presents the development of HESO-based electrocatalysts, focusing on (a) compositional tuning and (b) heterostructure fabrication. The synthesis conditions, evolution of material properties, and improvements in OER performance were thoroughly investigated and discussed. These findings make a significant contribution to the advancement of high entropy oxide-based electrocatalyst research. Therefore, it is recognized that the candidate is worthy of the degree of Doctor of Engineering.