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**Promotionsangelegenheiten**

Universitätsstraße 1  
40225 Düsseldorf  
Telefon: +49 (0)211 81 15092  
E-Mail: [promotionmnf@hhu.de](mailto:promotionmnf@hhu.de)

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Promotionsverfahren von **Frau M. Eng. Thi Hai Yen Beglau**  
**Auslage** der Dissertation und Gutachten sowie Termin der mündlichen Prüfung  
Anlage: Einseitige Zusammenfassung der Dissertation

Sehr geehrte Damen und Herren,

in dem oben genannten Promotionsverfahren wird die Annahme der Dissertation

**Bimetallic Metal-Organic Frameworks (MOFs) as Precursor Electrocatalysts for Enhancing the Oxygen Evolution Reaction (OER)**

von den Berichterstattenden Prof. Dr. C. Janiak und Prof. Dr. C. Ganter beantragt. Sie kann zusammen mit den Gutachten in der Zeit

**vom 19.07.2024 bis 05.08.2024**

eingesehen werden. Bitte wenden Sie sich zur Einsicht an das Promotionsbüro ([promotionmnf@hhu.de](mailto:promotionmnf@hhu.de)).

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Sofern die Dissertation angenommen wird, findet die mündliche Prüfung am

**08.08.2024 um 13:00 Uhr**

im **Hörsaal 6H** statt. Als Prüferinnen bzw. Prüfer sind vorgesehen:  
Juniorprof. Dr. M. Suta, Juniorprof. Dr. J. Meisner und Dr. B. Schmidt.

Die Öffentlichkeit ist bei der Befragung nicht zugelassen.

Mit freundlichen Grüßen  
im Auftrag

Amina Diekmann

Abstract of dissertation entitled  
Bimetallic Metal-Organic Frameworks (MOFs) as Precursor Electrocatalysts for Enhancing the  
Oxygen Evolution Reaction (OER)  
submitted by **Thi Hai Yen Beglau**

For a degree of Doctor of Philosophy (Ph.D.) in Natural Science the Faculty of Mathematics and  
Natural Sciences of Heinrich Heine University of Düsseldorf

The oxygen evolution reaction (OER), as the bottleneck of electrochemical activity, is extensively studied for efficient electrolytic water splitting. There is a need for innovative and cost-effective methods to prepare active and long-lasting electrocatalysts based on earth-abundant elements which holds promise for the development of efficient, practical and economical energy conversion materials for OER activity. Metal-organic frameworks (MOFs) are considered to be good precursors for active mixed-metal oxide/hydroxide electrocatalysts, as they allow to achieve a defined mixed-metal composition with a uniform distribution of metals at the nanoscale. A promising approach would be a one-step rapid synthesis of highly active electrocatalysts without energy-intensive carbonisation (pyrolysis) pretreatment.

In the first research focus of this work its bimetallic nickel-iron counterpart [Ni(Fe)(BDC)<sub>2</sub>DABCO], (BDC = 1,4-benzenedicarboxylate, DABCO = 1,4-diazabicyclo[2.2.2]octane) and their modified Ketjenblack (mKB) composites through a facile one-step solvothermal method. These materials were then evaluated for their performance in the OER in an alkaline medium (1 mol L<sup>-1</sup> KOH). The incorporation of a conductive mKB additive resulted in a synergistic effect, enhancing the catalytic activity of the MOF/mKB composites. Compared to individual MOFs and mKB, all MOF/mKB composite samples (7, 14, 22, 34 wt.% mKB) exhibited significantly improved OER performance. Notably, the NiMOF/mKB14 composite (14 wt.% mKB) demonstrated an overpotential of 294 mV at a current density of 10 mA cm<sup>-2</sup> and a Tafel slope of 32 mV dec<sup>-1</sup>, comparable to commercial RuO<sub>2</sub>, a benchmark material for OER. Further enhancement in catalytic performance was achieved with the Ni(Fe)MOF/mKB14 composite (0.57 wt% Fe), showing an overpotential of 279 mV at 10 mA cm<sup>-2</sup> and a low Tafel slope of 25 mV dec<sup>-1</sup>. Impregnating the Ni(Fe)MOF/mKB14 electrocatalyst into commercial nickel foam (NF) resulted in overpotentials of 291 mV and maintained for 30 h at 50 mA cm<sup>-2</sup>. Importantly, this work elucidates the in situ transformation of Ni(Fe)MOF into OER-active  $\alpha/\beta$ -Ni(OH)<sub>2</sub>,  $\beta/\gamma$ -NiOOH, and FeOOH with residual porosity inherited from the MOF structure, as confirmed by PXRD, FTIR, SEM and N<sub>2</sub> sorption analysis.

Furthermore, a series of monometallic Ni-, Co- and Zn-MOFs and bimetallic NiCo, NiZn- and CoZn-MOFs of formula M<sub>2</sub>(BDC)<sub>2</sub>DABCO and (M,M')<sub>2</sub>(BDC)<sub>2</sub>DABCO (M, M' = metal) with the same pillar and layer linkers DABCO and BDC were prepared through a fast microwave-assisted thermal conversion synthesis method (MW) within only 12 min. The mono- and bimetallic MOFs were selected to systematically explore the catalytic activity of their derived metal oxide/hydroxides for the OER. Among all tested bimetallic MOF-derived catalysts, the NiCoMOF exhibits superior catalytic activity for the OER with the lowest overpotentials of 301 mV and Tafel slopes of 42 mV dec<sup>-1</sup> in 1 mol L<sup>-1</sup> KOH electrolyte at 10 mA cm<sup>-2</sup>, which is comparable with commercial RuO<sub>2</sub> commonly used as a benchmark material for OER. In addition, NiCoMOF was in situ grown in just 25 min by the MW synthesis on the surface of NF with different mass loadings, where overpotentials of 313 and 328 mV at 50 and 300 mA cm<sup>-2</sup>, respectively, were delivered and superior long-term stability exists for practical OER application. The simple, rapid and controllable MW synthetic concept is very flexible and also can be extended to various structured materials including different types of MOFs to be applied for water-splitting, which has great potential for practical commercialization of the process as well.

The last research focus, we report two new isotopic semiconductive metal phosphonate frameworks Co<sub>2</sub>[1,4-NDPA] and Zn<sub>2</sub>[1,4-NDPA] (1,4-NDPA<sup>4-</sup> is 1,4-naphthalenediphosphonate). Co<sub>2</sub>[1,4-NDPA] and Zn<sub>2</sub>[1,4-NDPA] have optical bandgaps of 1.7 eV and 2.5 eV respectively, which are within the semiconductive regime. The electrocatalyst derived from Co<sub>2</sub>[1,4-NDPA] as a precatalyst generated an overpotential of 374 mV in the OER with a Tafel slope of 43 mV dec<sup>-1</sup> at 10 mA cm<sup>-2</sup> in the alkaline electrolyte (1 mol L<sup>-1</sup> KOH), which is indicative of remarkably superior reaction kinetics. The OER of Co<sub>2</sub>[1,4-NDPA] materials as precatalyst coupled with NF showed exceptional long-term stability at 50 mA cm<sup>-2</sup> for water splitting compared to the state-of-the-art Pt/C/RuO<sub>2</sub>@NF after 30 h in 1 mol L<sup>-1</sup> KOH.