2D transition metal–TCNQ sheets as bifunctional single-atom catalysts for oxygen reduction and evolution reaction (ORR/OER) - DTU Orbit (24/07/2019)

The identification of catalytically active and stable bifunctional electrocatalysts for the oxygen reduction and evolution reaction (ORR/OER) would revolutionize rechargeable metal-air batteries and regenerative fuel cell technologies. In this study, we use density functional theory (DFT) calculations to systemically investigate 2D transition metal based tetracyanoquinodimethane (TM–TCNQ, TM = Cr-Cu, Ru-Ag, Pt, Ir) monolayers with single TM atoms catalysts (SACs) distributed periodically with high density. We calculate a lower limiting overpotential of $\eta_{\text{lim}} = 0.33$ V for Fe-TCNQ yielding a higher expected activity than that of Pt metal (0.48 V) for the ORR under acidic conditions. The catalytic performance of Fe-TCNQ for OER is, however, surpassed by Ni-TCNQs ($\eta_{\text{lim}} = 0.46$ V), which is identified as the highest among the candidates. By applying grafting axial ligands and external strain, the adsorption strength of reaction intermediates on TM reactive sites can be further optimized and enhances the activities of Mn-, Fe- and Ni-TCNQs for the ORR or the OER. Here, Fe-TCNQ-Cl ($\eta_{\text{lim}} = 0.27$/0.55 V), followed by Fe-TCNQ-CO ($\eta_{\text{lim}} = 0.67$/0.43 V), are predicted as novel, high-performance bifunctional ORR/OER catalysts with comparable limiting overpotentials to those of the best commercially used electrocatalysts, Pt (ORR: $\eta_{\text{lim}} = 0.48$ V) and RuO$_2$ (OER: $\eta_{\text{lim}} = 0.42$ V). In addition, the recently synthesized Fe-TCNQ possess excellent conductivity with fast electron transfer during the catalytic reactions. These results show 2D TM-TCNQ monolayers are durable, low-cost, and efficient catalysts for the ORR and the OER in metal-air batteries and fuel cells.