

## 12th Workshop on Renewable Energy and Sustainability (WREN2024)

### Activity and stability of catalysts – A first Principles Study

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#### **Abstract:**

The electrochemical, as well as photo-electrochemical, conversion of CO<sub>2</sub> and H<sub>2</sub>O into fuels, such as methanol, ethanol, and H<sub>2</sub>, using metal or transition metal oxide catalysts, holds strong promise for renewable and sustainable fuel generation. However, the catalytic activity and catalyst stability under operating conditions are still major challenges to be addressed. In this presentation, I will discuss two different topics. The first one is polaron-mediated oxygen evolution reaction (OER) activity enhancement on the (110) surface of rutile TiO<sub>2</sub>, and the second one is copper cathodic corrosion during CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR).

**1<sup>st</sup> topic:** The focus of this study is rutile TiO<sub>2</sub>, a material extensively explored for solar energy conversion in artificial photosynthesis, with a specific emphasis on producing green H<sub>2</sub> through photoelectrochemical (PEC) H<sub>2</sub>O splitting. Using density functional theory (DFT) methods, we systematically investigate the impact of polarons on the oxygen evolution reaction (OER) on the (110) surface of rutile TiO<sub>2</sub>. Our theoretical exploration of polarons within the surface, along with simulations of OER at distinct titanium (Ti) and oxygen (O) active sites, reveals varying polaron formation energies at different lattice sites, with a strong preference for bulk and surface bridge oxygen (O<sub>b</sub>) sites. Furthermore, our research provides evidence of the facilitative role of polarons in OER. This study offers a detailed mechanistic insight into polaron-mediated OER, providing a promising approach to enhance the catalytic capabilities of transition metal oxide-based photocatalysts for meeting renewable energy requirements.

**2<sup>nd</sup> topic:** Electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) offers an efficient strategy to convert anthropogenic CO<sub>2</sub> gas into value-added fuels, such as hydrocarbons and alcohols. Up to now, copper (Cu) has been the primary choice as an electrocatalyst for CO<sub>2</sub>RR. However, Cu-based electrocatalysts have exhibited significant changes in structure and morphology, ultimately limiting their durability and stability. During CO<sub>2</sub>RR, surface Cu atoms undergo cathodic corrosion, causing them to leach out from the surface. The Cu dissolution mechanism during CO<sub>2</sub>RR remains a topic of debate

within the CO<sub>2</sub>RR community. In this study, our aim is to gain a detailed understanding of the thermodynamics and kinetics of Cu dissolution mechanisms during CO<sub>2</sub>RR, with the goal of designing a stable Cu catalyst that can operate reliably for extended periods, potentially lasting beyond several weeks. During this presentation, I will discuss in detail the combined influence of subsurface oxygen diffusion, the presence of OH<sup>-</sup> radicals on the surface, and the applied potential on Cu cathodic corrosion.