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Manganese oxide-based electrocatalysts for oxygen evolution reaction and electrochemical reforming of organic compounds in acidic media

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Over the past decade, the frequency of extreme climate events has increased due to rising greenhouse gas emissions, underscoring the urgency of decarbonizing energy systems and transitioning to sustainable sources. However, the intermittency of these sources necessitates efficient energy storage solutions. Hydrogen production, with the oxygen evolution reaction (OER) as the rate-determine step, presents a promising pathway. However, the most effective OER electrocatalysts rely on scarce, noble metals such as Pt, Ir, and Ru.[1]

In contrast, manganese oxides (MnO_x) offer a sustainable alternative due to their abundance, non-toxicity, and catalytic activity under acidic conditions - a critical environment for Proton exchange membrane electrolysers.[2] While manganese oxides can operate stably in acid up to 1.75 V_{RHE}, their stability beyond this potential is limited by the formation of permanganate ions and subsequent dissolution. To enable practical applications, it is crucial to improve the stability to extend the operational potential window. [3]

This study investigates the activity and stability of MnO_x and MnO_x combined with antimony, tin, titanium, niobium, and silicon oxides for OER. The most stable catalysts were further evaluated for the electrochemical reforming of small organic molecules - formic acid, methanol, ethanol, and ethylene glycol - using electrochemical mass spectrometry (EC-MS) to analyze gaseous products from the electrooxidation of these molecules and electrochemical infrared reflection absorption spectroscopy (EC – IRRAS) to investigate the formation of intermediates and gain deeper insights into the reaction mechanisms. Additionally, online inductively coupled plasma mass spectrometry (ICP – MS) was applied to assess catalyst dissolution.

Finally, we discuss the factors governing selectivity and stability for these species, offering insights into the development of more efficient, selective, and stable earth-abundant electrocatalysts for electrolysers.

[1] IRENA - International Renewable Energy Agency, Green Hydrogen cost reduction scaling up electrolyser to meet the 1.5°C climate goal. 2020
[2] P. Wang et al., Manganese-based oxide electrocatalysts for the oxygen evolution reaction: a review. Feb. 17, 2023, Royal Society of Chemistry.
[3] A. Li et al., “Stable Potential Windows for Long-Term Electrocatalysis by Manganese Oxides Under Acidic Conditions,” Angewandte Chemie - International Edition, vol. 58, no. 15, pp. 5054–5058, Apr. 2019.