

Role of oxygen vacancies δ in $\text{LiMn}_2\text{O}_{4-\delta}$ on stabilization of Mn dissolution during water oxidation

Omeshwari Y. Bisen^{1,2}, M. Risch^{1,2}

¹Nachwuchsgruppe Gestaltung des Sauerstoffentwicklungsmechanismus, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, 14109 Berlin, Germany

²Institut für Materialphysik, Georg-August-Universität Göttingen, Germany

Email: omeshwari.bisen@phys.uni-goettingen.de

Water splitting provides an attractive avenue for chemical energy storage by producing the green hydrogen, but it suffers from the inefficiency of the oxygen evolution reaction (OER) and the degradation of the electrocatalyst under the harsh oxidizing conditions of the reaction, particularly for manganese oxides. [1] Understanding these degradation processes is crucial. [1] Our previous studies used LiMn_2O_4 as a model system for OER in alkaline media, [2, 3, 4, 5] highlighting the role of Mn^{4+} species in dissolution, which we controlled before the onset of the OER by experimental design, i.e., the conditioning procedure. [2] In present study, we aimed to stabilize the system by tuning the bulk electronic structure via oxygen deficiency, creating $\text{LiMn}_2\text{O}_{4-\delta}$. X-ray photoelectron spectroscopy (XPS) (Fig. 1a) confirmed oxygen vacancy formation through a higher Mn/O ratio as compare to pristine particles, also supported by thermogravimetric analysis. Using a rotating ring-disk electrode (RRDE), we measured manganese corrosion and oxygen evolution by applying the desired detection potential at the Pt ring (Fig. 1b). We observed reduced Mn loss in $\text{LiMn}_2\text{O}_{4-\delta}$ compared to LiMn_2O_4 (Fig. 1c), indicating the beneficial role of oxygen vacancies. Therefore, it's highly desirable to investigate the role of oxygen deficiency on OER and understand the stability for the knowledge-guided design of stable OER catalysts.

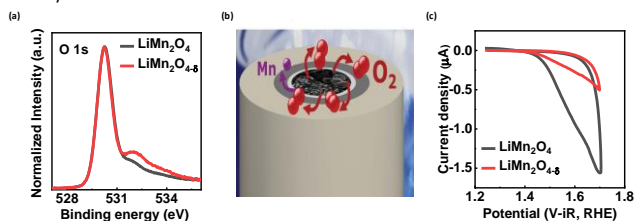


Figure 1: (a) O 1s HRXPS of pristine LiMn_2O_4 and oxygen deficient $\text{LiMn}_2\text{O}_{4-\delta}$ particles. (b) RRDE two electrode setup where Pt ring detects dissolved Mn and OER current at potential 1.2 V and 0.4 V vs RHE, respectively [Ref [4]]. (c) Dissolved Mn current observed at ring for LiMn_2O_4 and $\text{LiMn}_2\text{O}_{4-\delta}$ particles.

References: [1] M. Risch, *Current Opinion in Electrochemistry* 2023, 38:101247, DOI: 10.1016/j.coelec.2023.101247; [2] O. Bisen et al., *Energy Adv.*, 2024, **3**, 504-514, DOI:10.1039/D3YA00434A; [3] M. Baumung et al., *ChemPhysChem* 2019, 20, 2981-2988, DOI: 10.1002/cphc.201900601; [4] M. Baumung et al., *Sustain. Energy Fuels* 2019, 3, 2218-2226, DOI: 10.1039/c8se00551f; [5] F. Schönwald et al. arXiv:2007.04217v1