

Ruthenium and Iridium Pyrochlores as Catalysts for Oxygen Evolution Reaction (OER)

The electrochemical formation of the hydrogen is prerequisite to catalysis based storage of the renewable electricity. Water electrolysis being the only prospective source of hydrogen fully outlines the importance of the water splitting catalysts optimization which is, surprisingly, far more acute in the case of oxygen evolution reaction. Catalysis of the OER is rather difficult to optimize due to the well-known scaling relation restriction.¹

Practical solutions in water electrolysis can either aim at breaking the restrictions imposed by the volcano curve predictions (i.e. searching for a better OER catalysts) or one may entertain a more practical approach addressing the feasibility of the OER catalysts. In such an effort, one may either optimize (i.e. decrease) the scarce catalyst components or improve the catalysts stability namely in acid media, where the state of the art catalysts are based on iridium oxides.

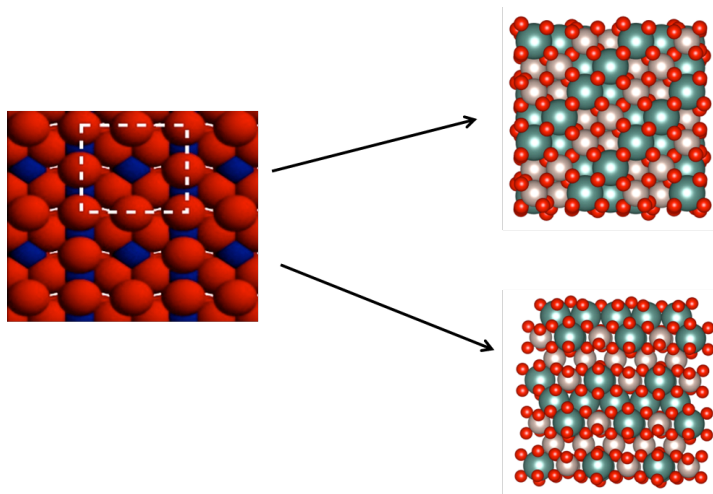


Figure 1 Structure of the (110) oriented rutile type oxide along with (100) (top right) and (110) (bottom right) projected pyrochlore surface structures.

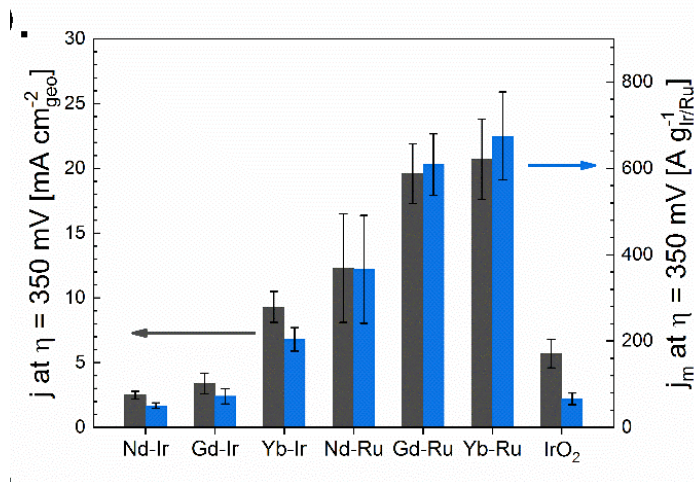


Figure 2 Measured OER activities for several Ru and Ir based pyrochlores featuring Ru or Ir in the B site.

A decrease of noble metal content can be conveniently achieved if one moves from tetragonal oxides of rutile type (typical for RuO₂ and IrO₂) to cubic pyrochlores of the A₂B₂O₇ type. In this arrangement, one may expect the surface structure to deviate just moderately from those of rutile or perovskite investigated previously.

The cubic pyrochlore structure is highly flexible and can exist for different combinations of A-site and B-site cations. The smaller cation typically resides in the B-site. For catalytically active Ru or Ir occupying B-sites, the A-sites can be occupied by, e.g. lanthanides the size of which can control the d-band center unit cell parameter by controlling the metal-to-metal distance between the transition metal cations. The d band center position in turn is responsible for the anticipated OER activity.

This trend can be conveniently demonstrated on the Ru and Ir pyrochlores containing Yb, Gd and Nd. Such materials show a profound variability of the OER activity which improves with increasing overlap of the B site cation transition metals.

The pyrochlore structure is also improving the stability of the catalyst in the oxygen evolution process – in contrast to the activity, however, a convenient ratio of the A and B site cation needs to be achieved.

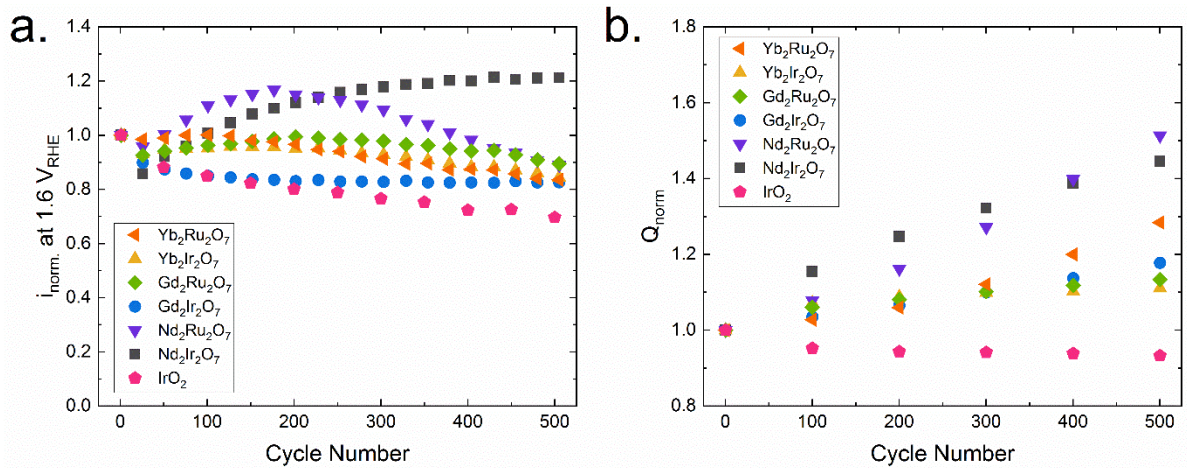


Figure 1. Electrochemical stability measurements for the pyrochlore samples showing the normalized current density at 1.6 VRHE (a) and the normalized surface charge calculated from cyclic voltammograms recorded after every 100 potential-step cycles (b) as a function of potential-step cycle number.

This work is based on the results of R. Pittkowski in collaboration with PSI Villigen and DTU Lyngby

References

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