Ruthenium-based pyrochlores as anodic electroctalysts for PEM water electrolysis

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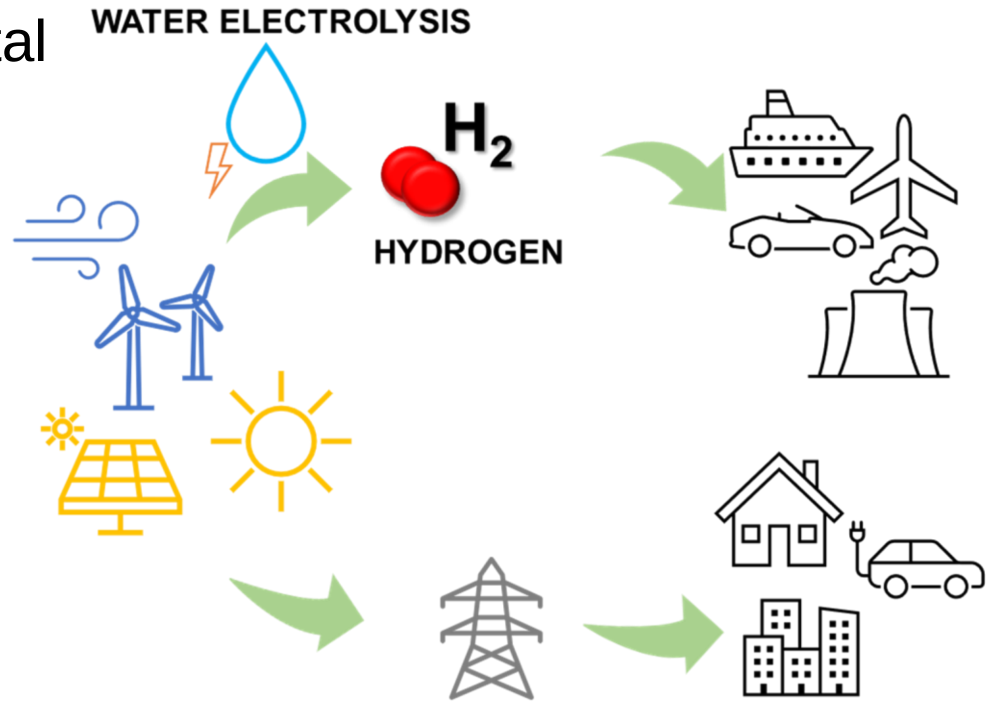
4 September 2023

Background

- The price of renewable energies has become comparable and even cheaper than fossil fuels due to the boom in production over the past decades
- Renewable energies are intermittent
- Conversion and storage is vital
- Hydrogen as energy carrier can/will play an integral role



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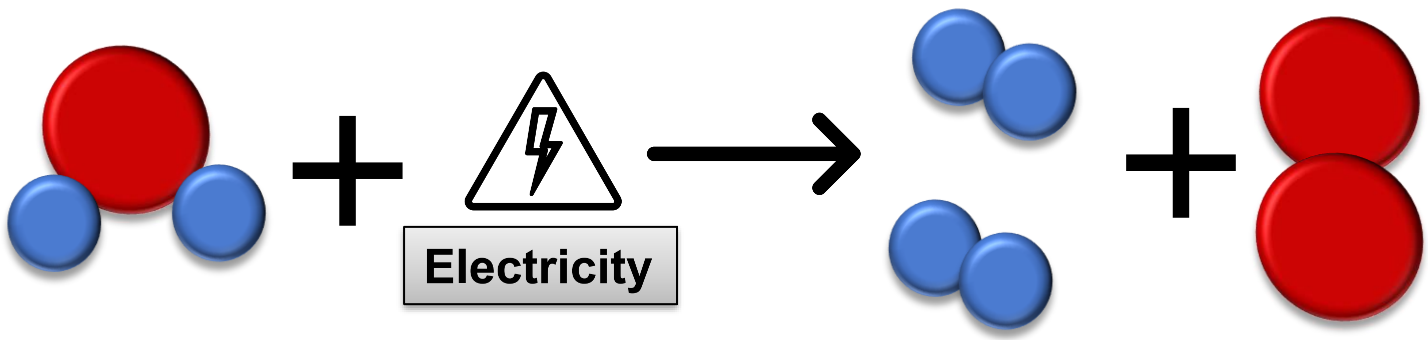


$2H_2O$ $2H_2$ O_2

Water electrolysis (WE)

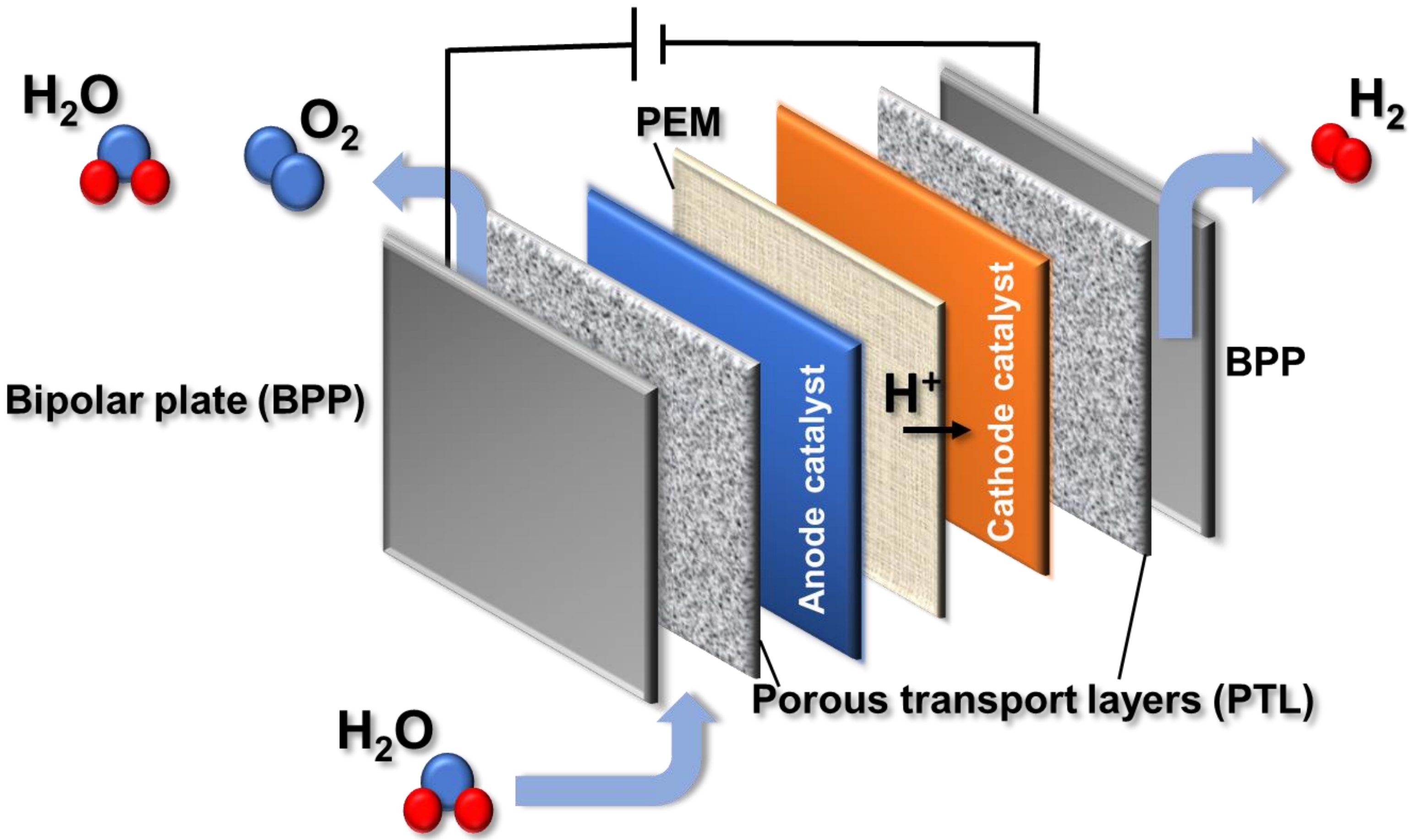
Background

Hydrogen production through PEM water electrolysis (PEMWE) is:

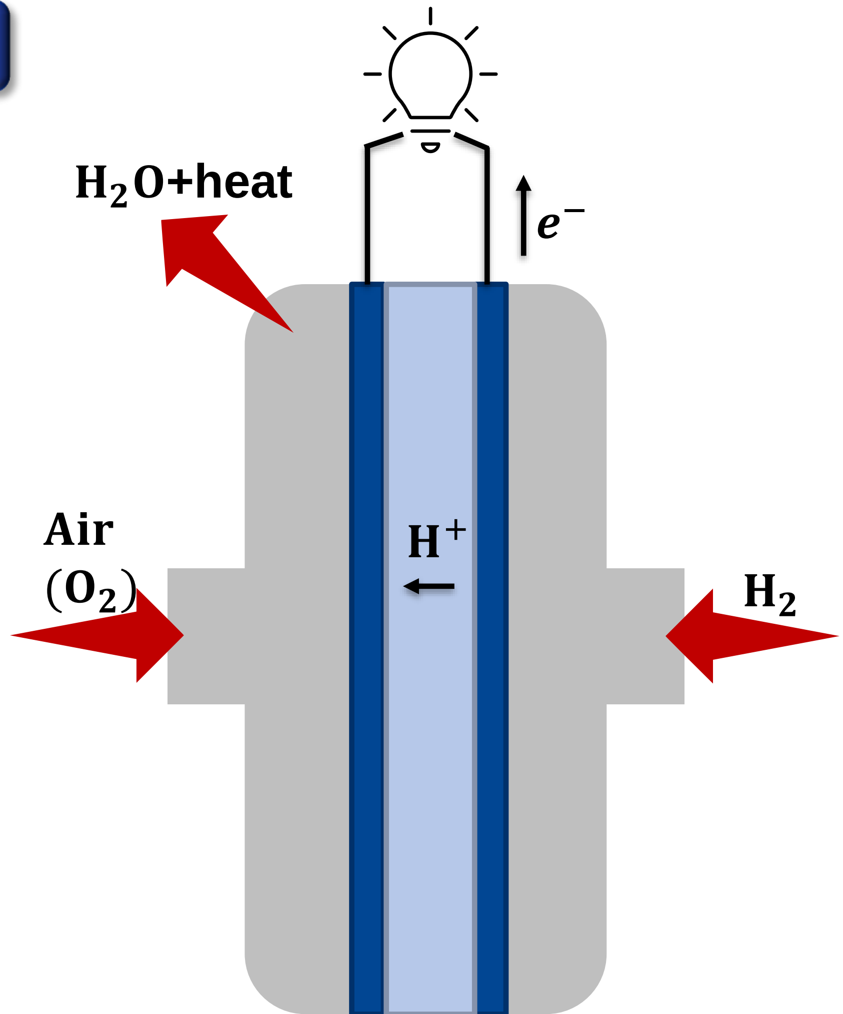
- Flexible and compact
- Energy efficient
- Able to function with load changes

However, expensive and scarce Ir used as state-of-the-art anodic electrocatalyst limits the large-scale implementation.

Background


H_2O
O_2
PEM
H_2
Bipolar plate (BPP)
Anode catalyst
H^+
Cathode catalyst
BPP
Porous transport layers (PTL)
H_2O

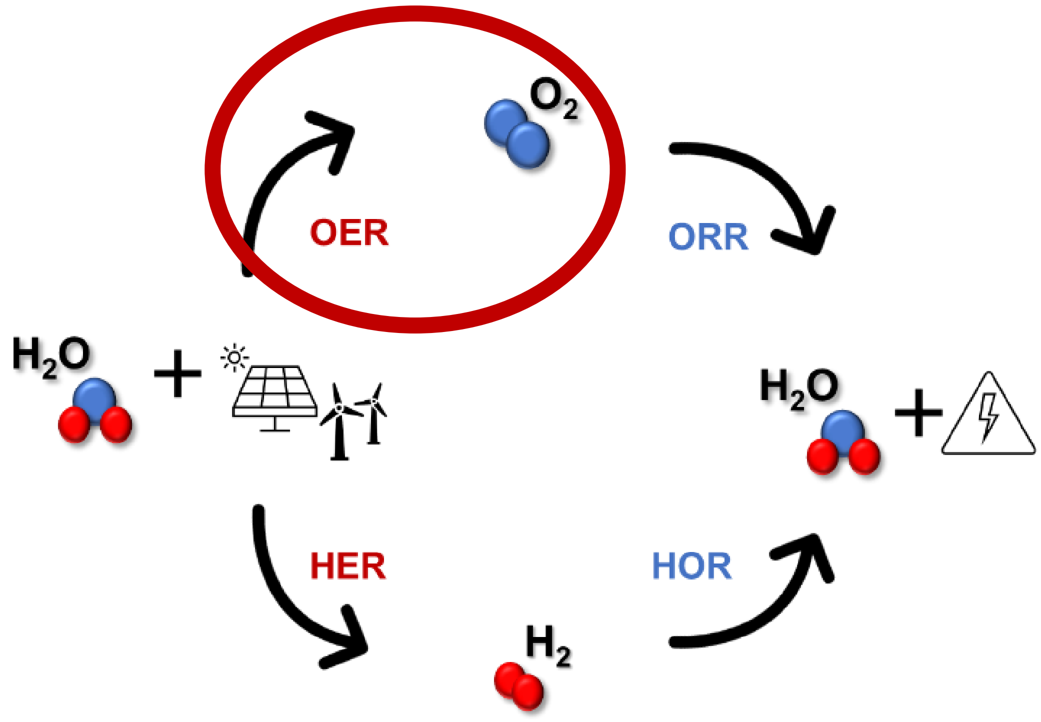
Background



$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

$$H_2 \rightarrow 2H^+ + 2e^-$$

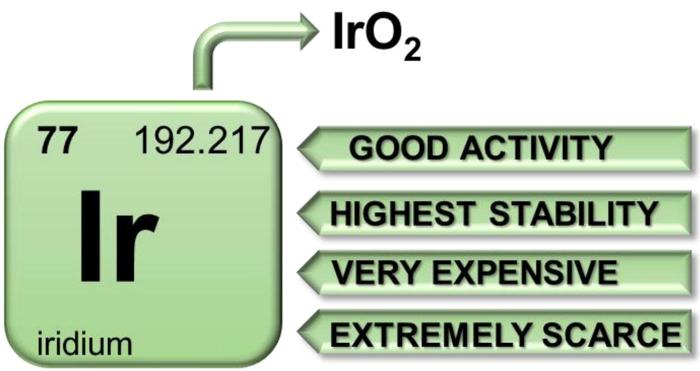
Background

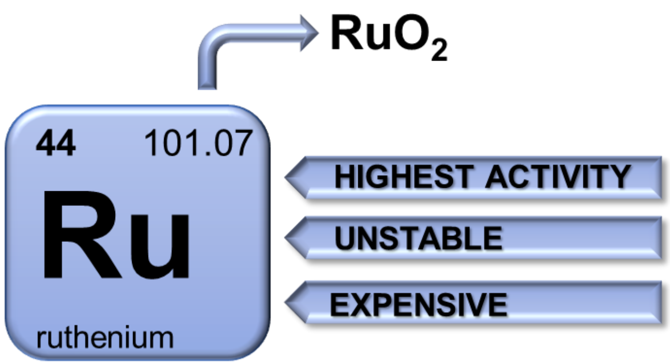


A schematic illustration of the different reactions involved in water splitting and conversion

Background

- A stable and active electrocatalyst is needed for the OER before the PEM technology can be widely implemented
- IrO_2 and RuO_2 are the state-of-the art electrocatalysts for the anodic OER.
- Ru is unstable in acid and the need for Ir will soon far exceed its worldwide production.





Background

- Ruthenium pyrochlores could be a viable solution, since they show promising activities[1,2].

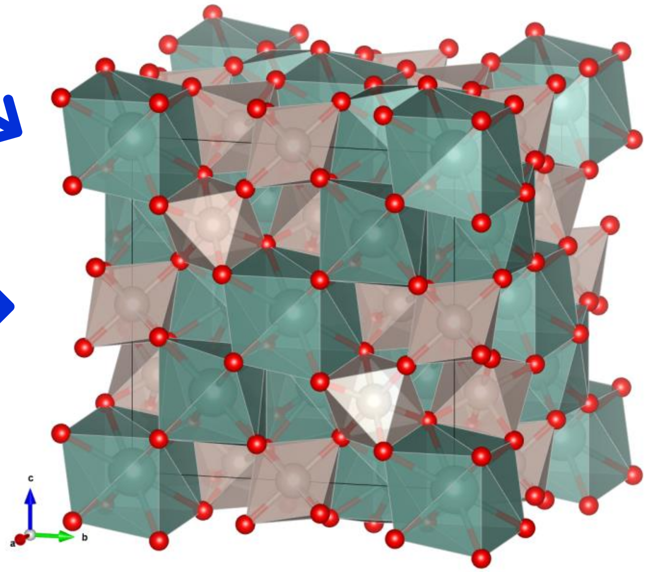
(1) Feng, Q.; Wang, Q.; Zhang, Z.; Xiong, Y.; Li, H.; Yao, Y.; Yuan, X.-Z.; Williams, M. C.; Gu, M.; Chen, H. Highly Active and Stable Ruthenate Pyrochlore for Enhanced Oxygen Evolution Reaction in Acidic Medium Electrolysis. *Appl. Catal. B Environ.* **2019**, *244*, 494–501.

(2) Kim, J.; Shih, P.-C.; Tsao, K.-C.; Pan, Y.-T.; Yin, X.; Sun, C.-J.; Yang, H. High-Performance Pyrochlore-Type Yttrium Ruthenate Electrocatalyst for Oxygen Evolution Reaction in Acidic Media. *J. Am. Chem. Soc.* **2017**, *139* (34), 12076–12083.

Background

Changing/doping the A-site

Changing/doping the B-site



Activity

Stability

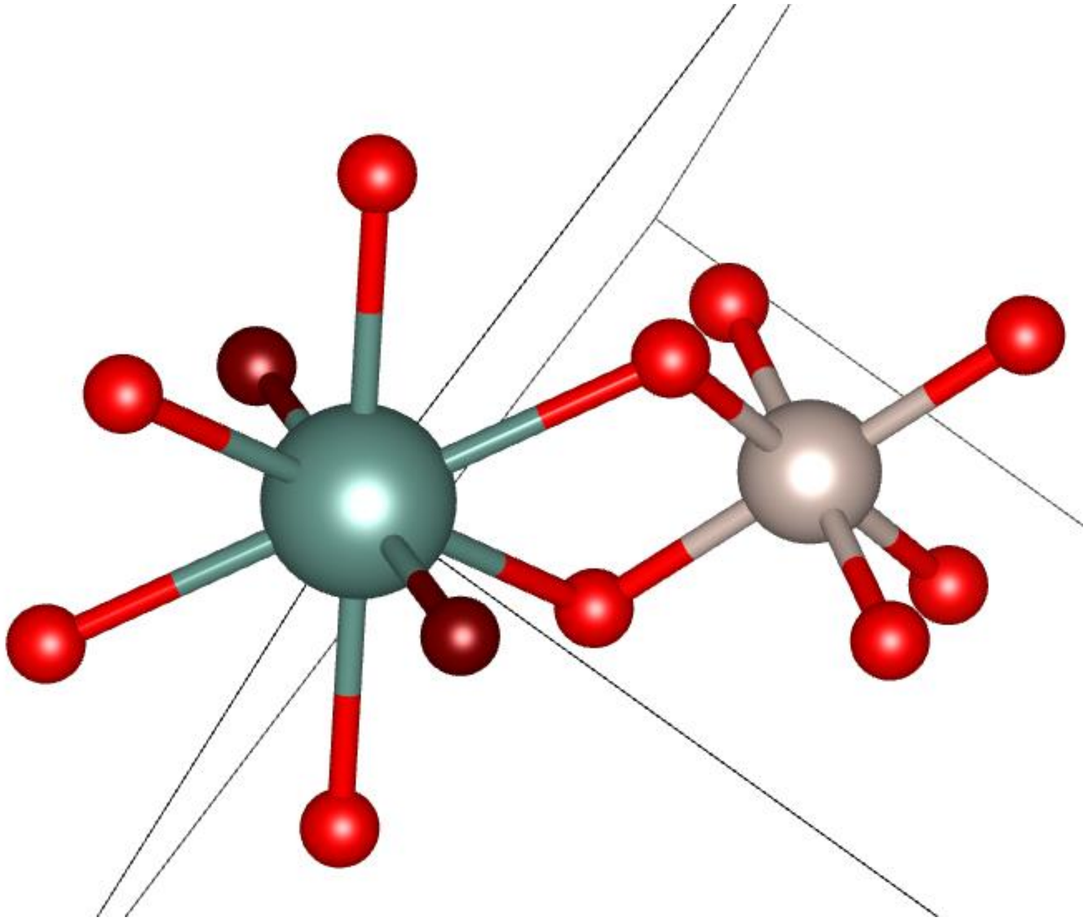
Conductivity

Different A- and B-site cations and dopants affect the activity, stability and conductivity, allowing a fine-tuned electrocatalyst.

Background

- The larger A-site cation is eight-fold coordinated in a distorted cube with six O anions equally spaced and two O` anions. (3+ charged)

- The B cations are six-fold coordinated. Two O`` vacant sites can also be present. (4+ charged)

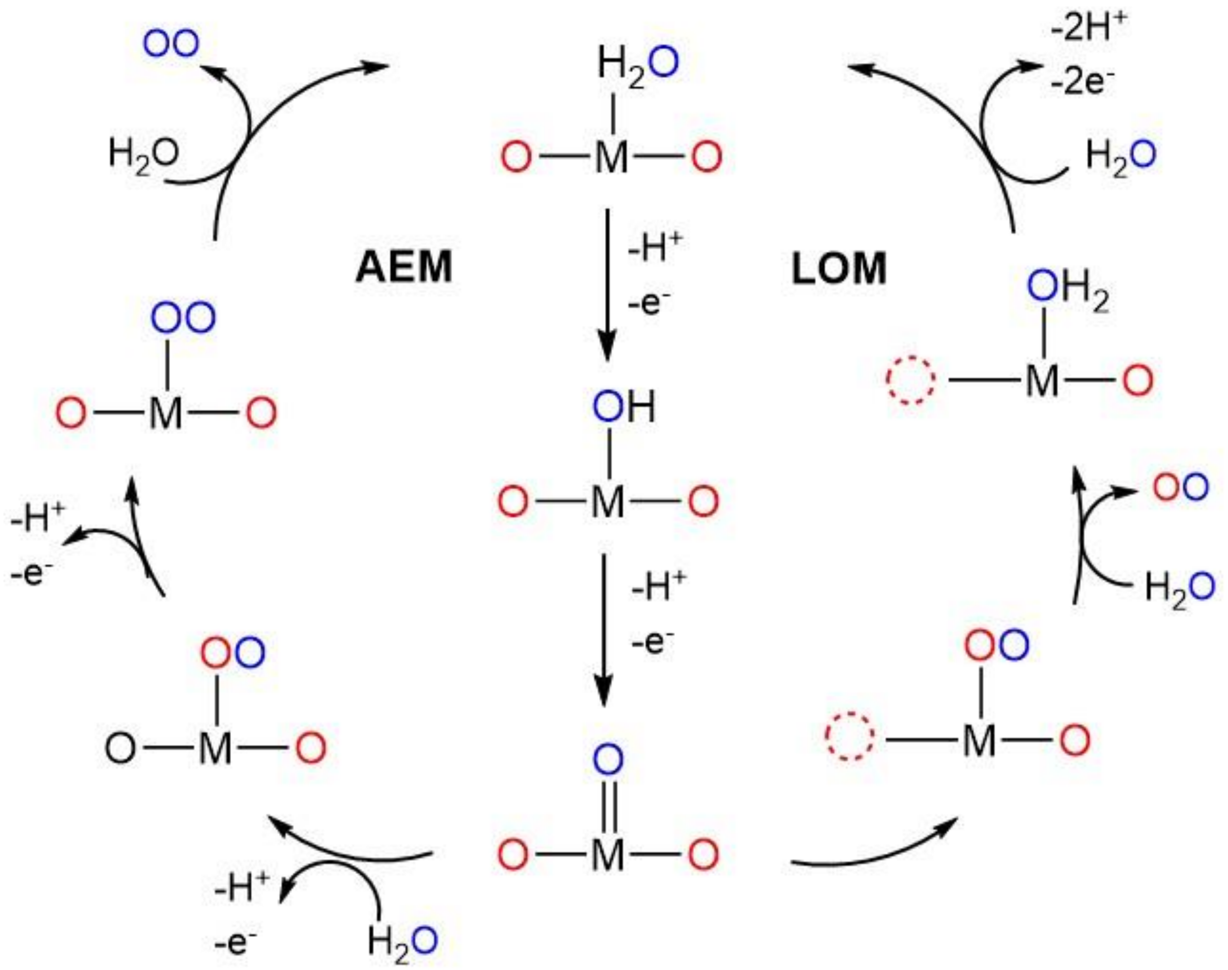


OER mechanism

- Various OER mechanisms have been postulated
- The pyrochlores are said to involve lattice oxygen participation in the mechanism, which could impact the stability

(3) D. A. Kuznetsov, M. A. Naeem, P. V Kumar, P. M. Abdala, A. Fedorov, C. R. Müller, *J. Am. Chem. Soc.* **2020**, *142*, 7883–7888.

Background



(3) D. A. Kuznetsov, M. A. Naeem, P. V Kumar, P. M. Abdala, A. Fedorov, C. R. Müller, *J. Am. Chem. Soc.* **2020**, *142*, 7883–7888.

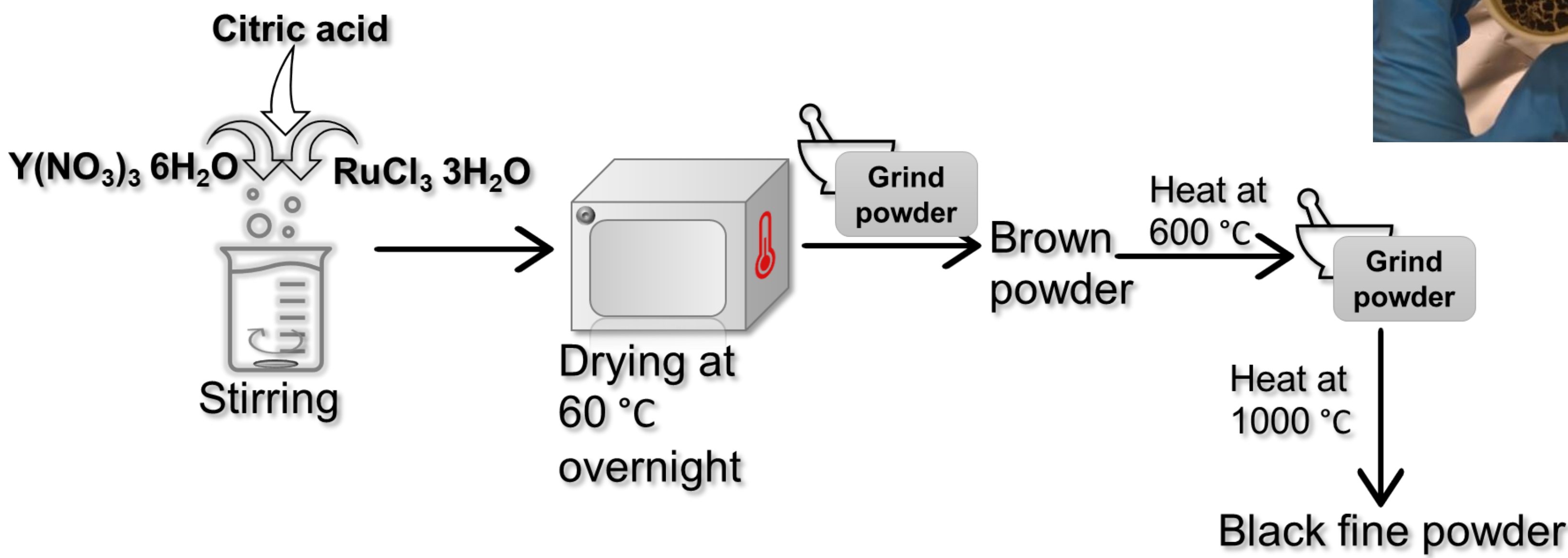
Introduction

HOPE

Revolutionizing Green Hydrogen Production with Next Generation PEM Water Electrolyser Electrodes

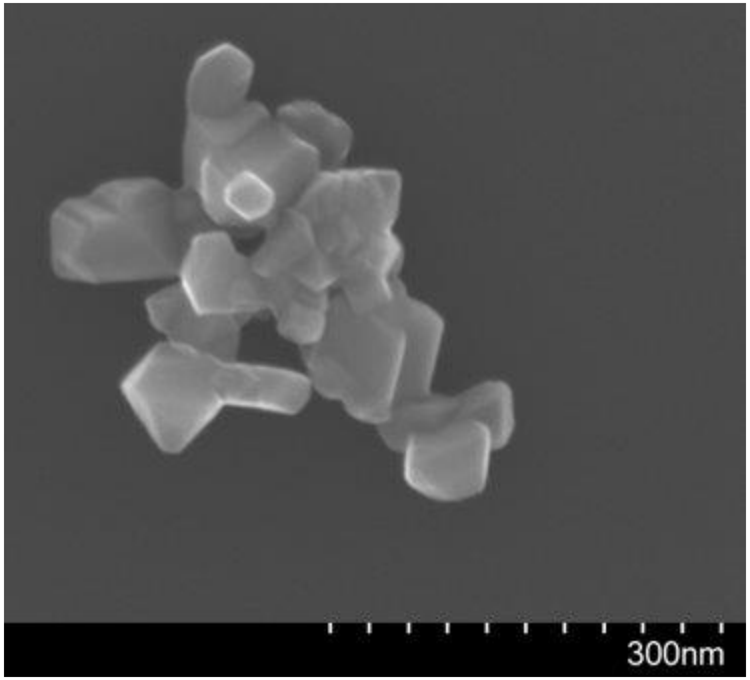
- Synthesis of $Y_2Ru_2O_7$ pyrochlores by a citrate synthesis method
- Doping in the A-site with transition metals

Synthesis method

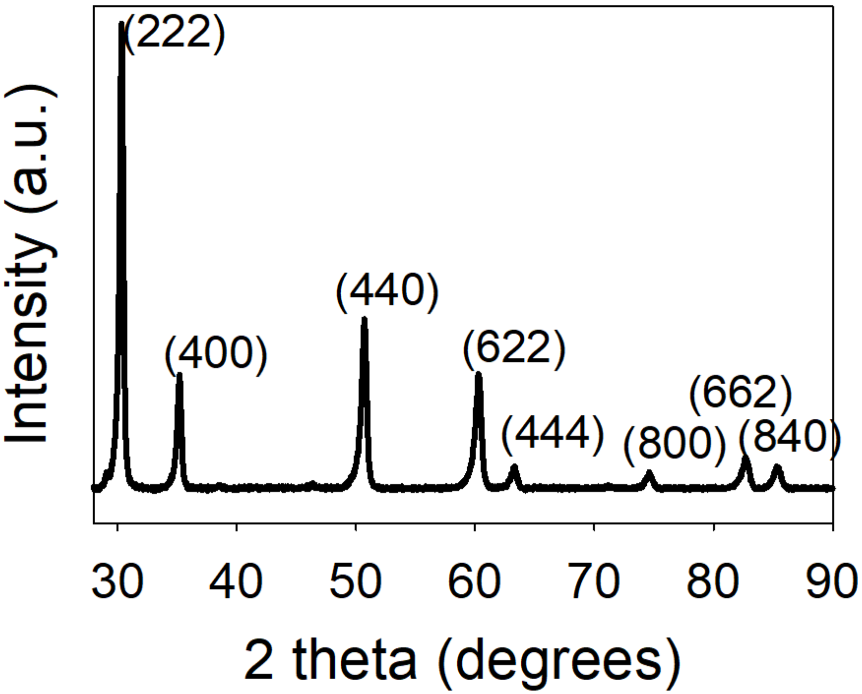


NTNU

Results

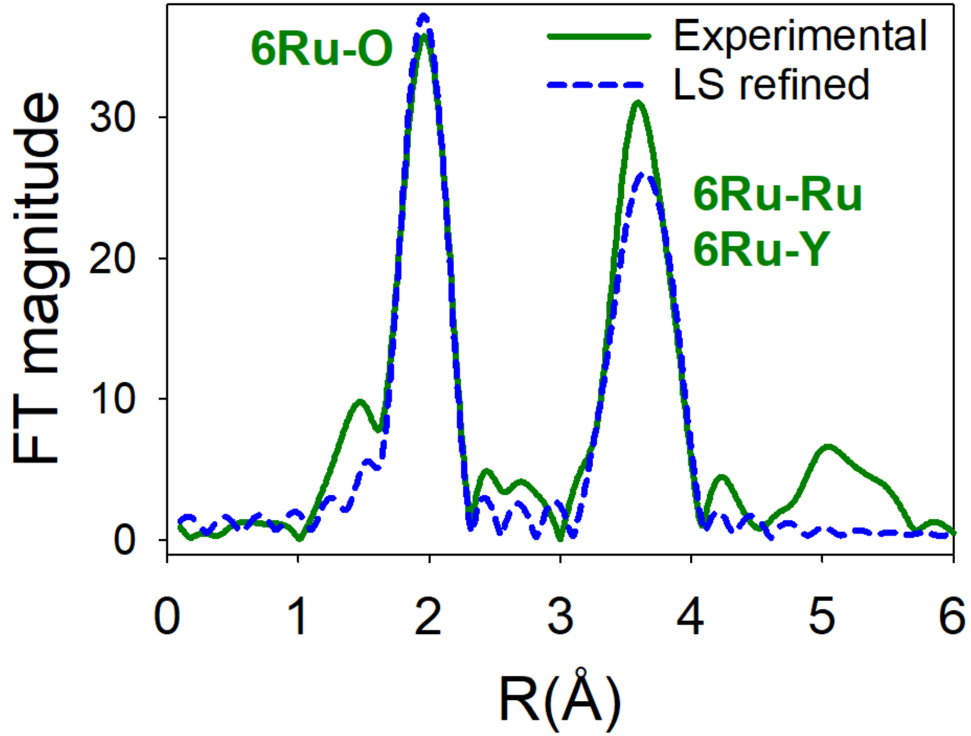


S(T)EM image of the $Y_2Ru_2O_{7-d}$ (calcined at 600 °C for 6 hours and 1050 °C for 9 hours)



X-ray diffractogram of the $Y_2Ru_2O_{7-d}$ (calcined at 600 °C for 6 hours and 1050 °C for 9 hours)

Results



Fourier-transform of the Ru K-edge EXAFS functions.

R 39.81

1	(RU)	R0	0.000
2	(O)	R1	1.993
3	(Y)	R2	3.626
1	(RU)	R3	3.817

From Kuznetsov *et al*. :

Ru-O	3.632(6)
Ru-M	1.988(6)

(3) D. A. Kuznetsov, M. A. Naeem, P. V Kumar, P. M. Abdala, A. Fedorov, C. R. Müller, *J. Am. Chem. Soc.* **2020**, *142*, 7883–7888.

3-electrode ex-situ testing

- RDE WE (1600 rpm), RHE RE and Pt CE
- Tested weather activation CVs has an effect on activity
- Tafel
- CVs to analyse electrochemical behavior
- Preliminary stability testing (800 CVs between 1.4-1.6 V)
- Compared with commercial iridium oxide (ECSA estimation used for normalization)

Ink preparation

- 10 mg powder
- 475µL DI-water (Milli-Q, 18.2MΩcm)
- 475µL isopropyl alcohol (IPA) (technical, VWR)
- 50µL Nafion 117 (5 wt%, Sigma Aldrich)
- 20 minutes of sonication, no ice

- 10 µL was drop-casted onto a GC.

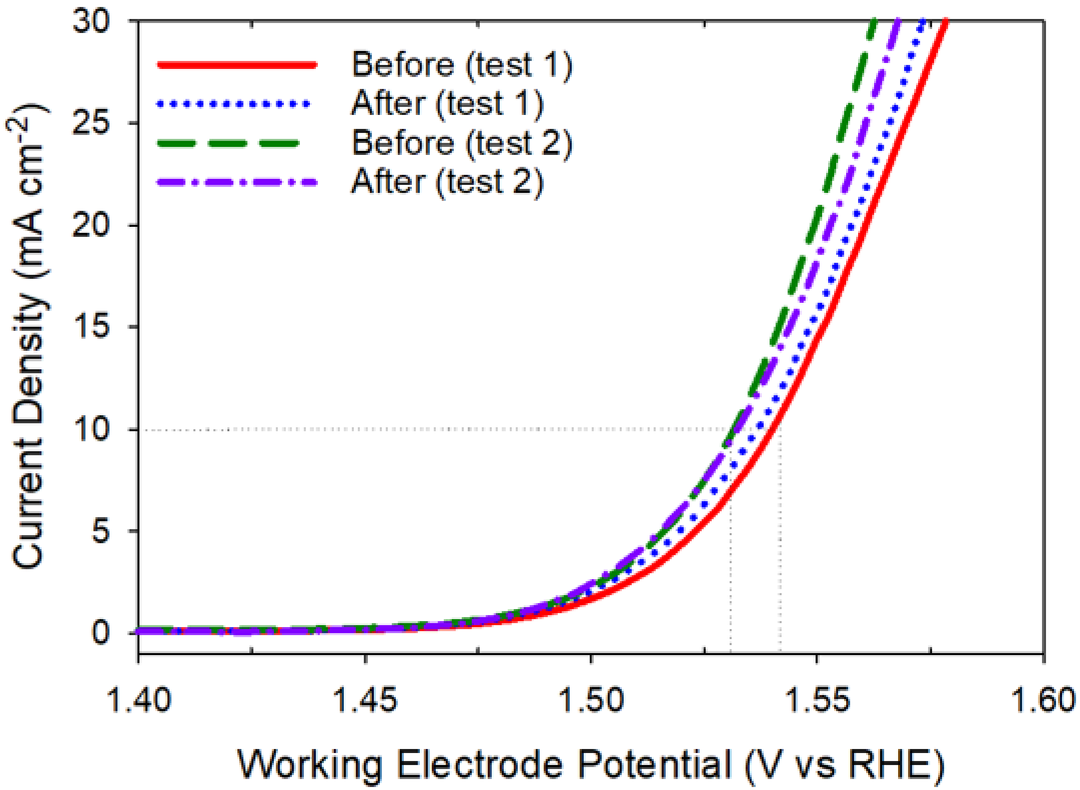
Results

• 20 CVs were performed after an initial LSV to see if the electrocatalysts need to be preconditioned/activated

• The activity remains almost the same regardless of activation CVs

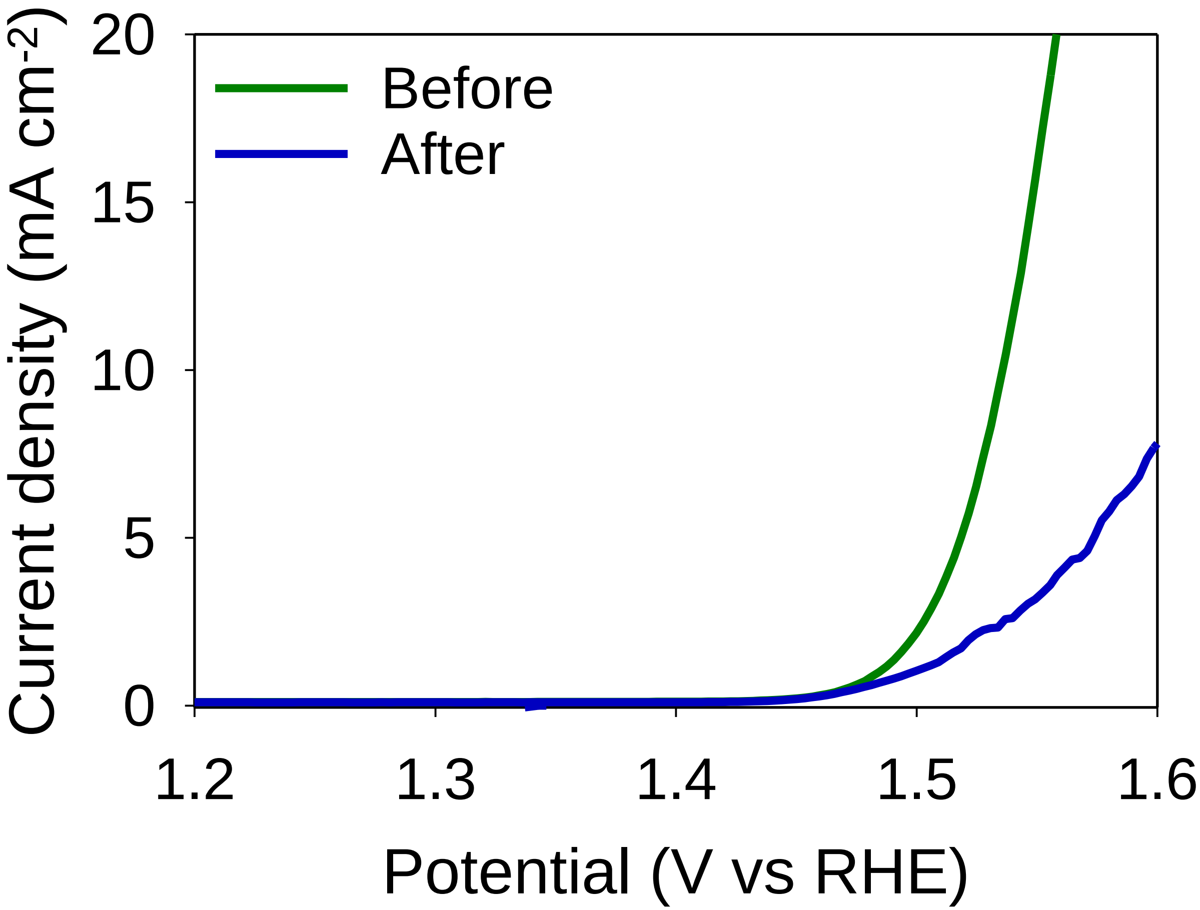
• The activity as observed from the LSV correlates well with literature

•The Tafel slope of this electrocatalyst is calculated as 42 mV/dec



LSVs of $Y_2Ru_2O_{7-d}$ (loading of 5 mg cm^{-2}) before and after activation CVs

Results



Stability screening of $Y_2Ru_2O_7$. LSV before (green) and after (blue) 800 CVs between 1.4 and 1.6 V.

Results

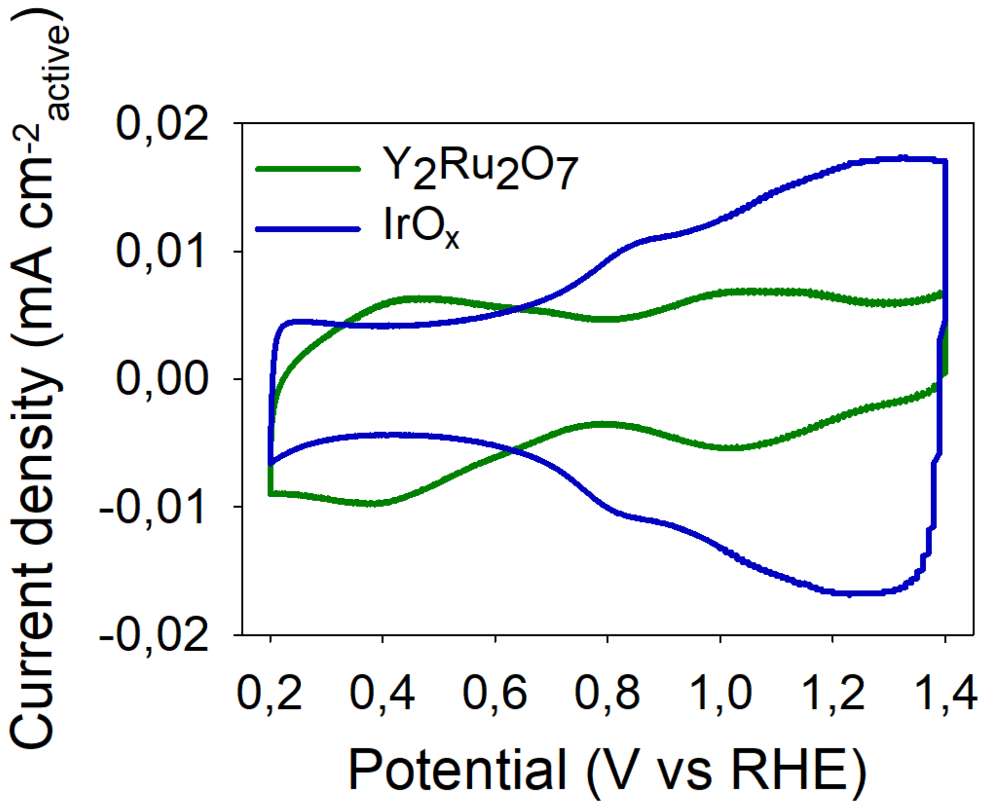
- The double layer capacitance was used to be able to compare the activity of $Y_2Ru_2O_7$ to that of commercial IrO_2
- Cyclic voltammograms at different scan-rates were obtained in a non-faradaic region and straight-line plots of current density versus scan-rates were obtained where the slope yielded the double layer capacitance
- This is not claimed as the true active surface area of these catalysts but is used to convey a trend and allow us to compare the activities roughly

(4) Feng, Q.; Zhang, Z.; Huang, H.; Yao, K.; Fan, J.; Zeng, L.; Williams, M. C.; Li, H.; Wang, H. An Effective Strategy to Tune the Oxygen Vacancy of Pyrochlore Oxides for Electrochemical Energy Storage and Conversion Systems. *Chem. Eng. J.* **2020**, *395*, 124428. https://doi.org/https://doi.org/10.1016/j.cej.2020.124428.

(5) Obradović, M. D.; Balanč, B. D.; Lačnjevac, U. Č.; Gojković, S. L. Electrochemically Deposited Iridium-Oxide: Estimation of Intrinsic Activity and Stability in Oxygen Evolution in Acid Solution. *J. Electroanal. Chem.* **2021**, *881*, 114944. https://doi.org/https://doi.org/10.1016/j.jelechem.2020.114944.

(6) Faustini, M.; Giraud, M.; Jones, D.; Rozière, J.; Dupont, M.; Porter, T. R.; Nowak, S.; Bahri, M.; Ersen, O.; Sanchez, C. Hierarchically Structured Ultraporous Iridium-based Materials: A Novel Catalyst Architecture for Proton Exchange Membrane Water Electrolyzers. *Adv. Energy Mater.* **2019**, *9* (4), 1802136.

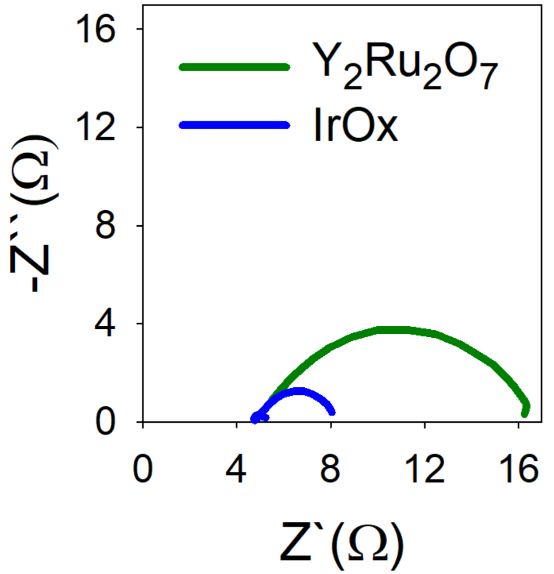
Results

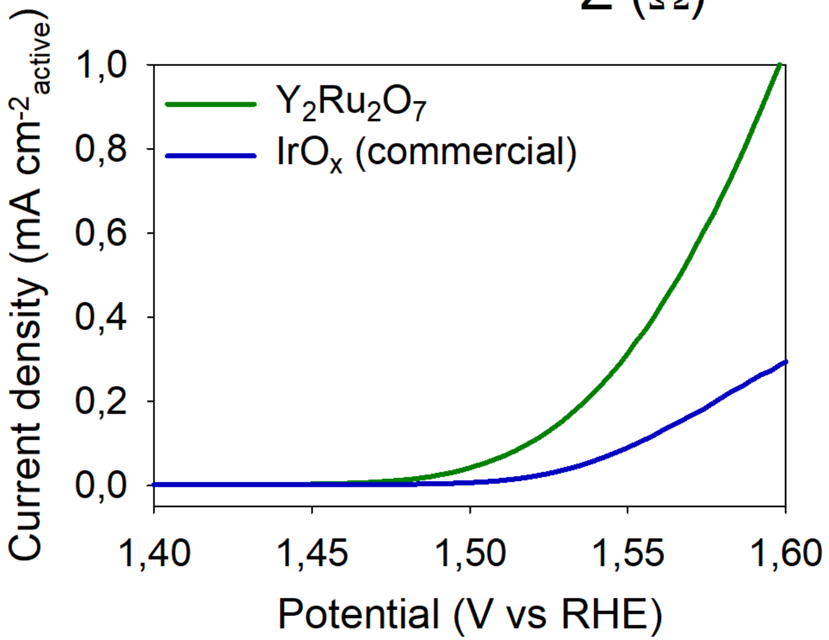


CVs of $Y_2Ru_2O_7$ and IrO_x

Results

- The active-area normalised activity of $Y_2Ru_2O_7$ is higher than that of commercial IrO_2
- The charge-transfer resistance of IrO_2 is half of that of $Y_2Ru_2O_7$, indicating that conductivity improvements is needed

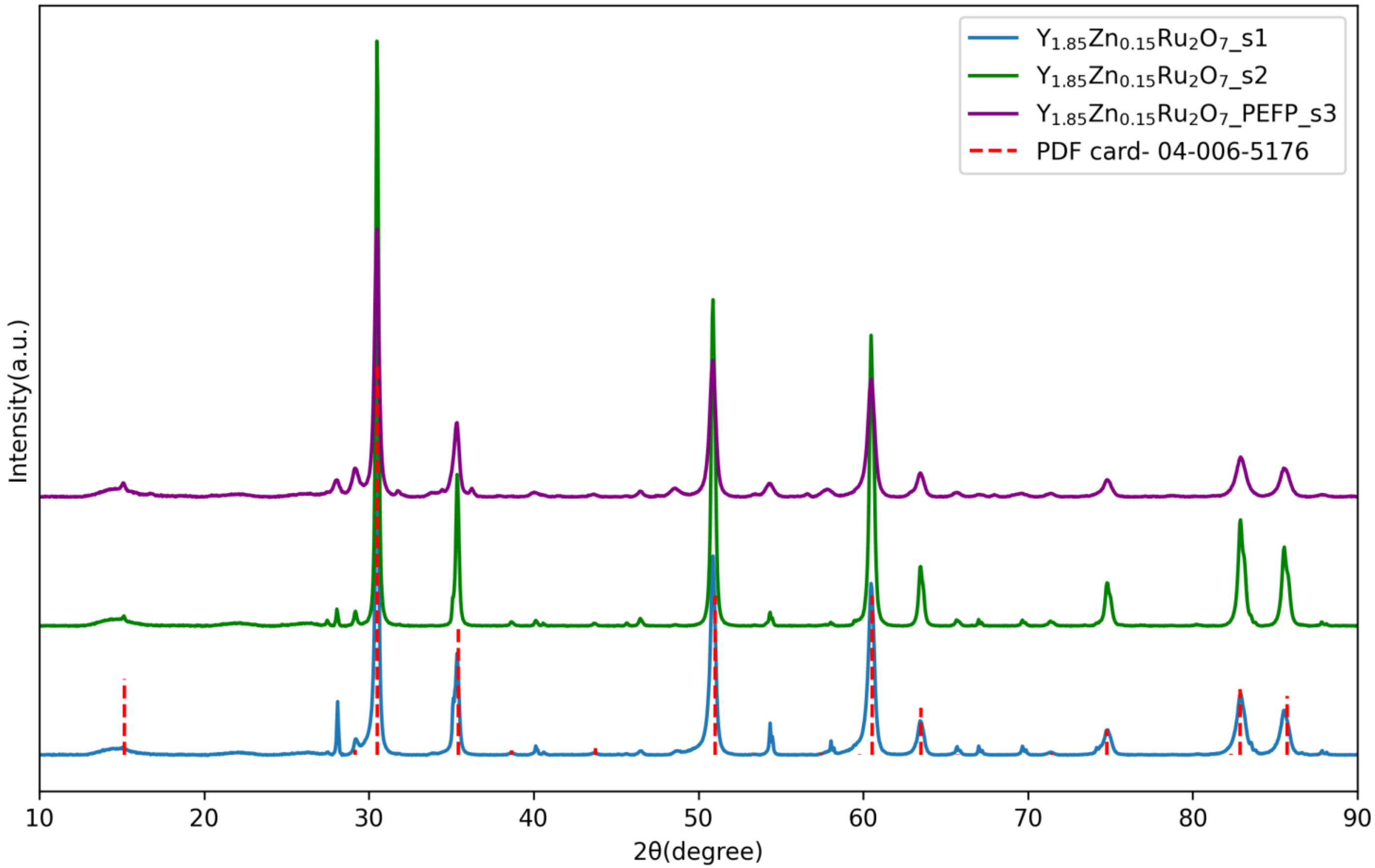




LSVs of $Y_2Ru_2O_{7-d}$ and IrO_x

Challenges

- We are currently struggling with phase purity of doped samples and samples prepared with a modified synthesis method



Future plans

- Optimise particle size with milling and/or alternative synthesis routes.
- Optimise conductivity through doping and test conductivity with 4-point probe
- Investigate the band-gap through diffuse reflectance spectroscopy
- Establish a half-cell testing method to better bridge the gap between 3-electrode testing and full-cell tests

Questions and discussions