

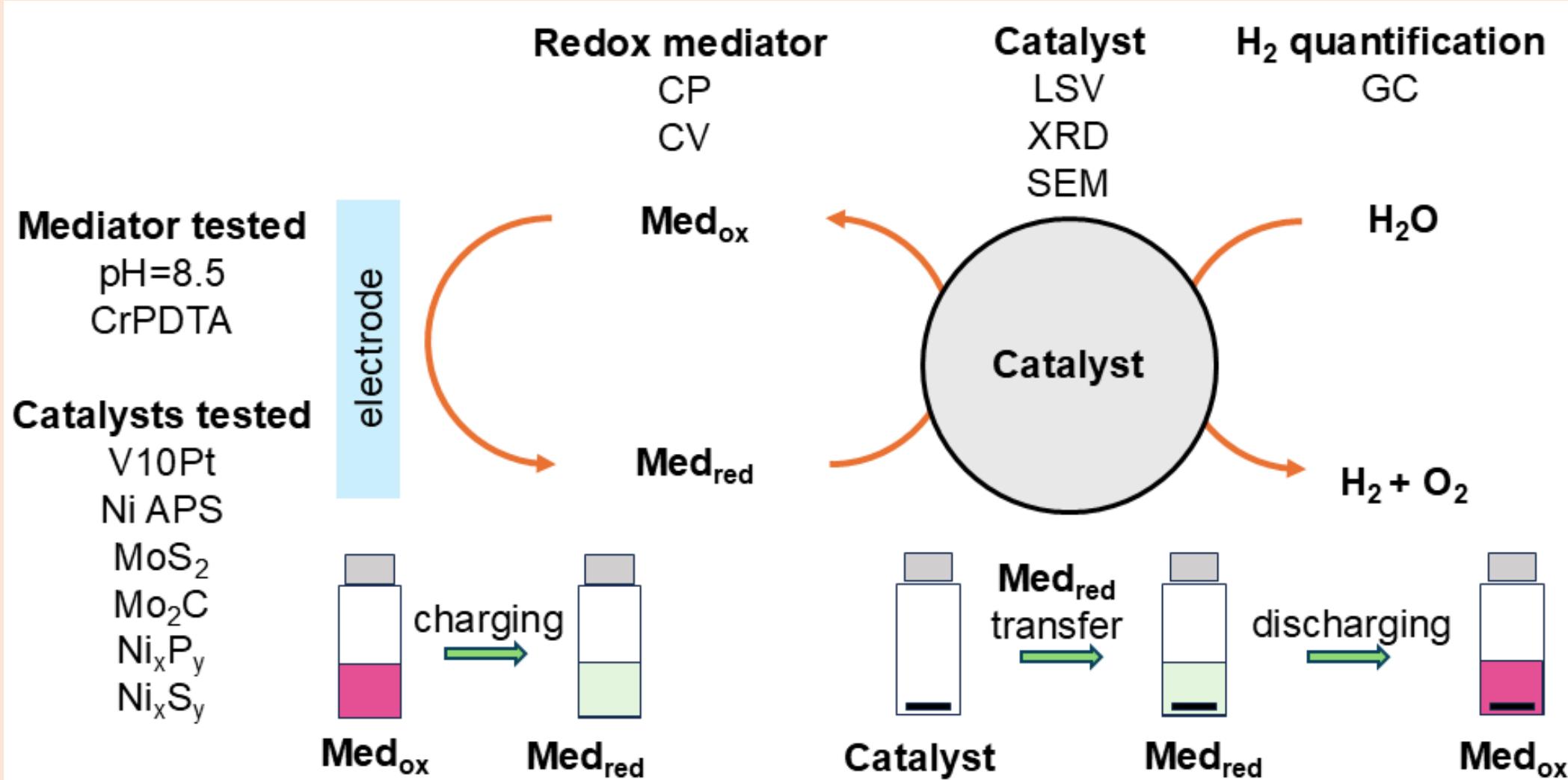
Evaluating Non-Platinum Group Catalysts for Decoupled Water Splitting in Bicarbonate Buffer



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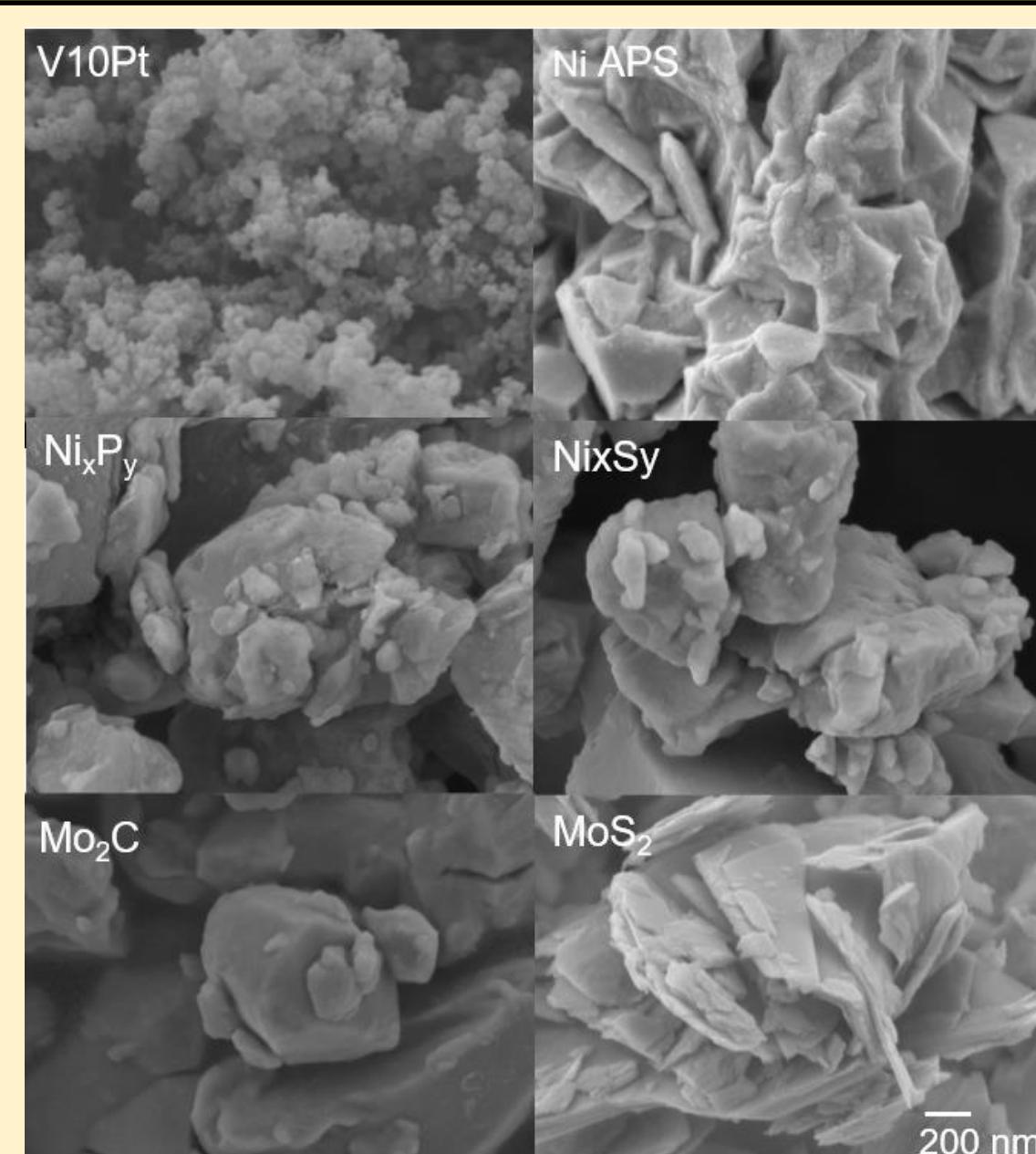


1. Abstract



- Electrochemical water splitting is crucial for the **decarbonization of industrial processes** and the coupling of **renewable energy** sources.
- Conventional H₂O electrolyzers** generate H₂ and O₂ in neighbouring compartments using critical raw materials (CRMs) as catalysts and corrosive electrolytes, which raises issues (**cost and safety**)
- We use **redox mediators** as electrical **charge and potential vectors** to separate catalytic product formation from the electrode surface.
- We report the successful application of **decoupled electrolysis in near-neutral pH** using **bicarbonate buffer**.
- MoS₂** gives the highest faradaic yield of all electrocatalysts
- We evaluate the **kinetics** and **thermodynamics** of the decoupled HER

2. Materials



SEM shows:

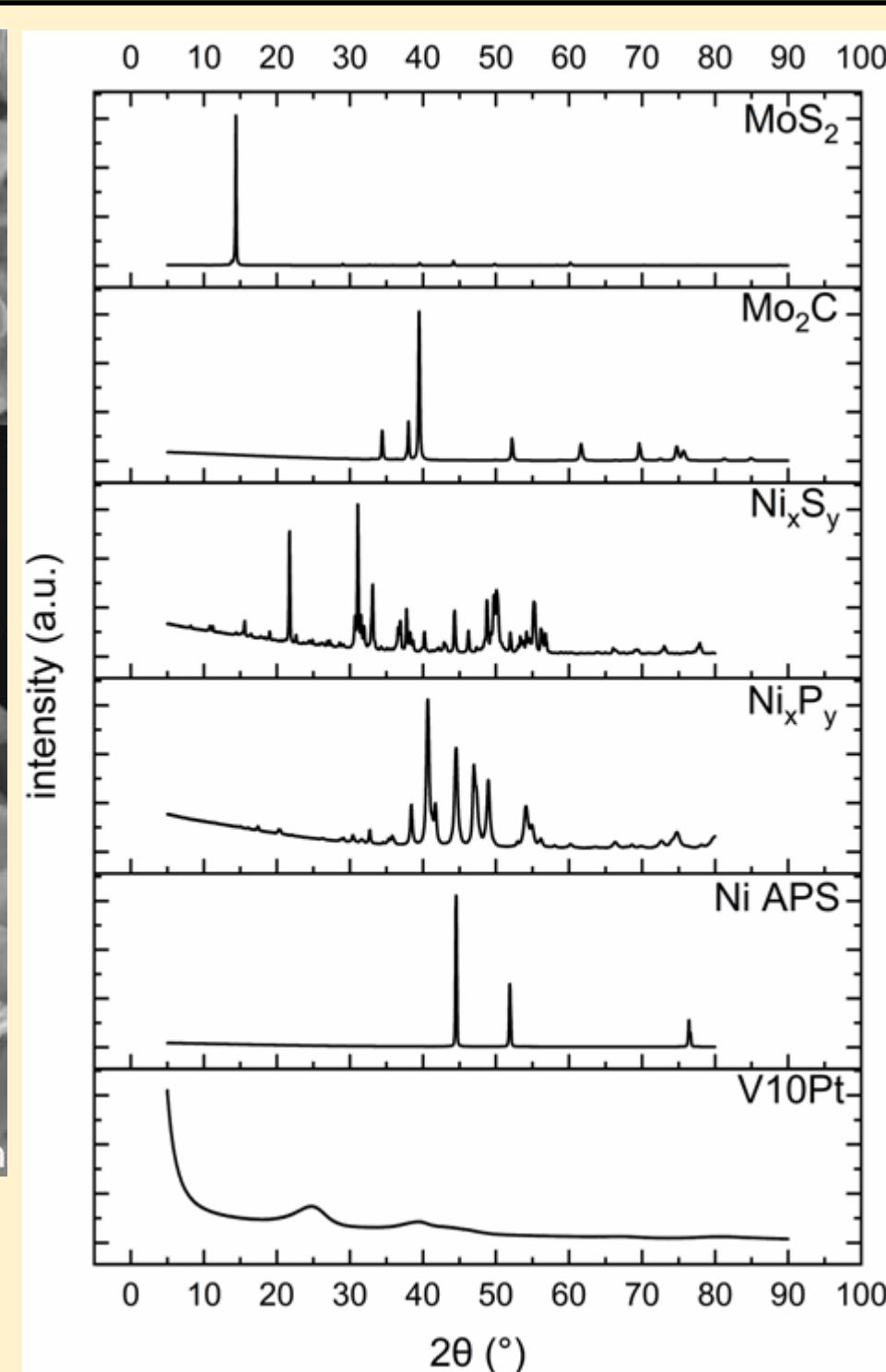
Mo₂C → large bulk particles of 1-5 μ m size with a smooth surface

MoS₂ → few-layer MoS₂ nanosheets, 20-90 nm thick

Ni_xP_y and **Ni_xS_y** → larger particles of 1-10 μ m together with smaller size particles with irregular shape with a coarse surface.

Ni APS → agglomerates of 3-7 μ m particles with smaller size particles with rough surface consisting of 10 nm-thick platelets.

V10Pt → graphitized carbon spheres of about 20 nm size in a very dispersed, coarse and low-density structure.



PXRD shows:

Mo₂C → hexagonal β -form

MoS₂ → hexagonal 2H-phase

Ni_xS_y → Ni₃S₂ (heazlewoodite), Ni₃S₄ (polydimide)

Ni_xP_y → Ni₂P, Ni₅P₄, possibly Ni₁₂P₅

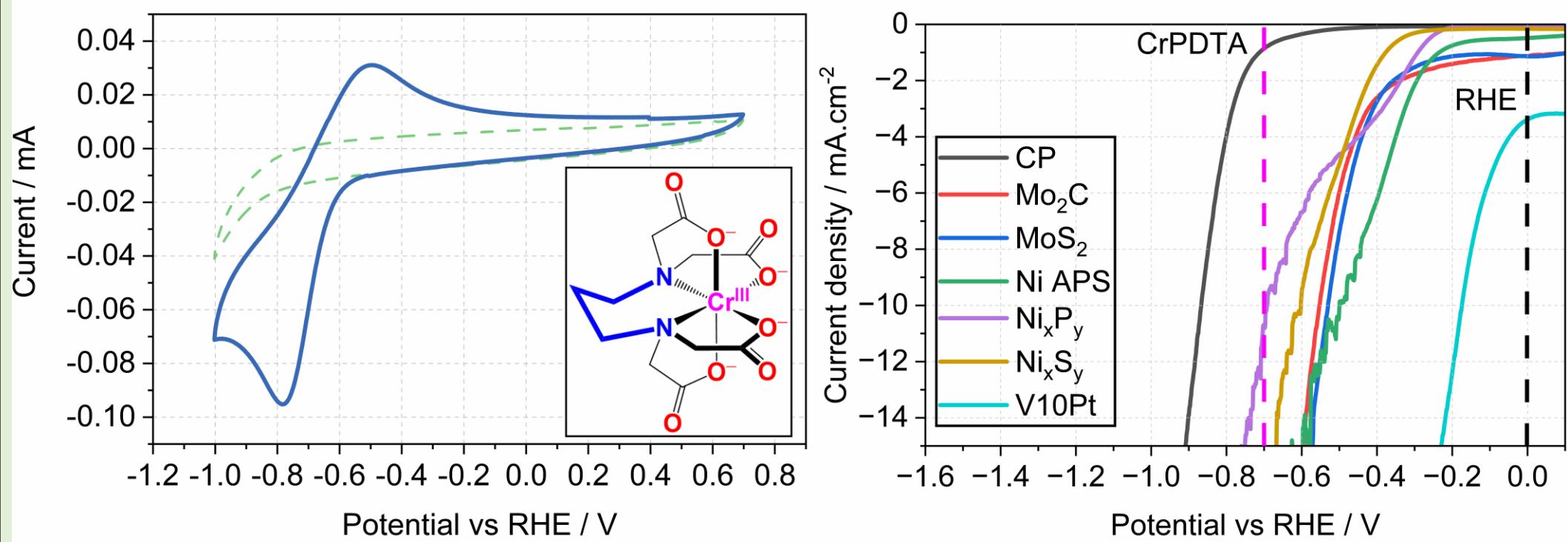
Ni APS → fcc bulk metal structure

V10Pt → fcc structure of well-dispersed Pt, together with amorphous carbon

6. References

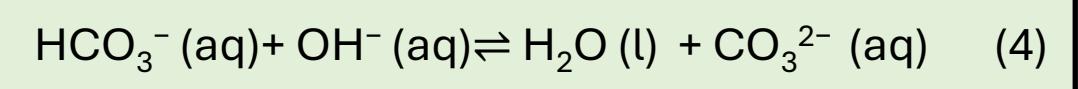
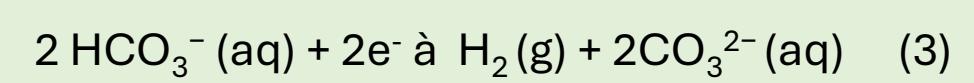
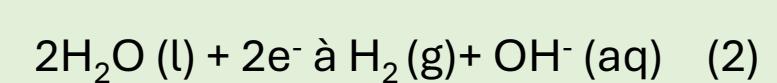
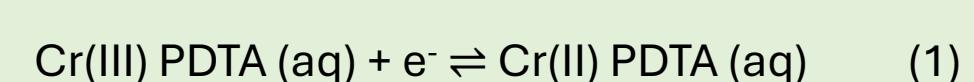
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3. Electrochemical characterisation

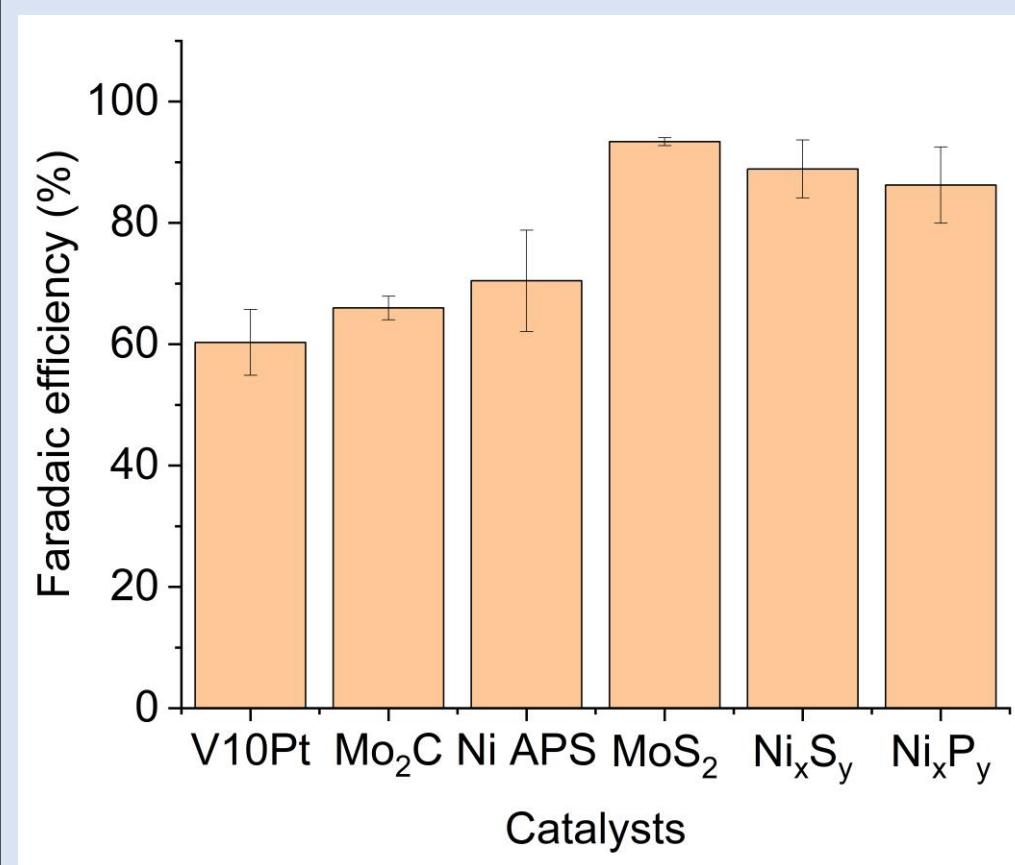


- The combination of a large driving force and a near neutral pH gives Cr PDTA (**chromium 1,3 propanediamine-N,N,N',N'-tetraacetic acid**) a very large potential **over the thermodynamic requirement** (overpotential of 0.7 V) to enable the redox mediated HER (eqn (2-4)).
- Bicarbonate buffer can also contribute towards the HER (eqn (3-4)).
- The reduced CrPDTA can **spontaneously evolve hydrogen** in the presence of all the

electrocatalyst materials since the half wave potential of the mediator is more negative than the HER onset potential of all the catalysts.

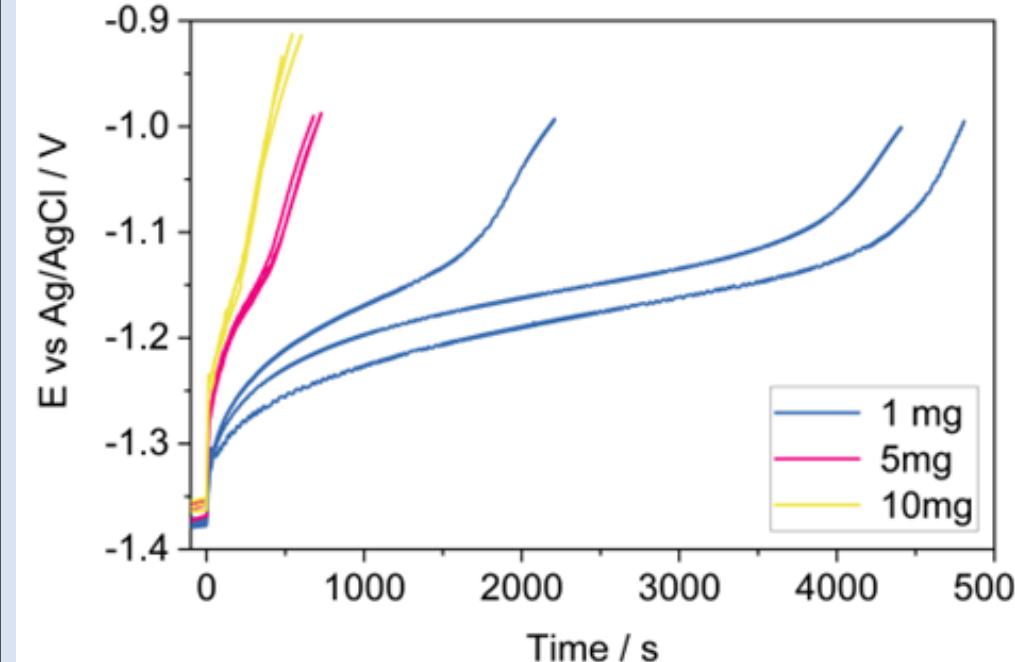


4. Catalytic activity and kinetics characterisation



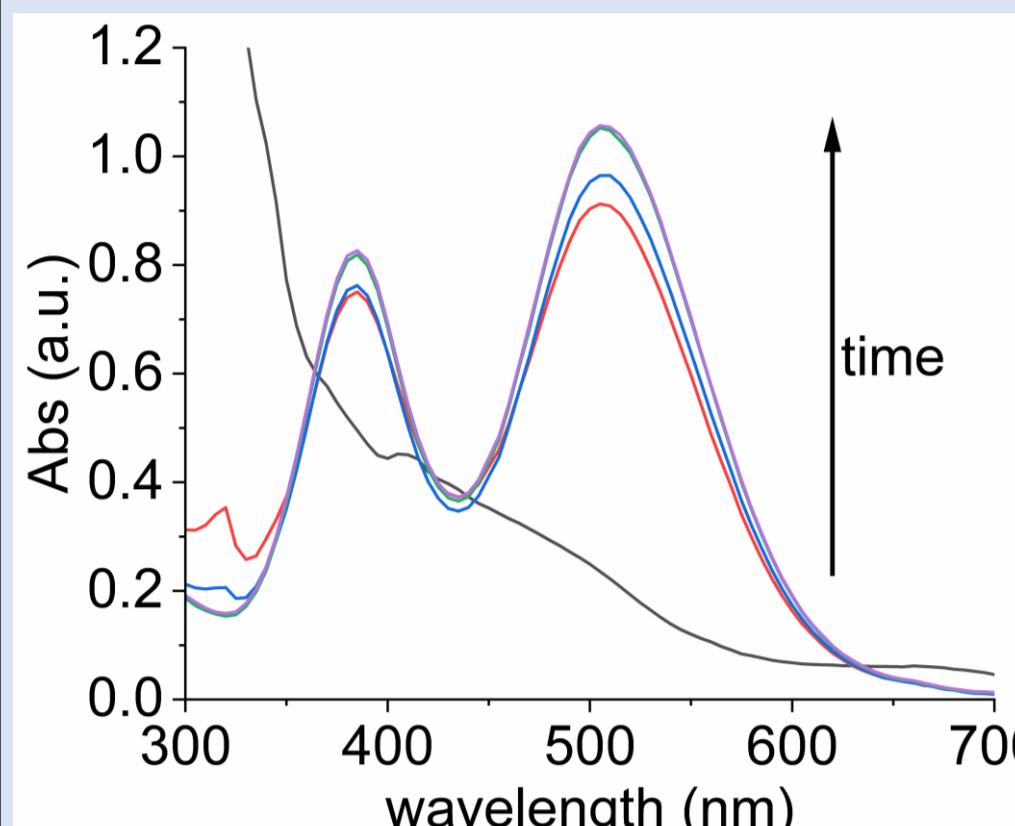
Faradaic yields:

- MoS₂ gave the highest H₂ yield (93.39 ± 0.66)
- MoS₂ is followed by Ni_xS_y and Ni_xP_y (88.89 ± 4.77 and 86.23 ± 6.29 , respectively)
- Ni APS shows the most variable response (average yield of $70.45 \pm 8.35\%$)
- Mo₂C gave a consistently low response of $65.975 \pm 1.95\%$
- V10Pt catalyst used for comparison gave the lowest yield of $60.29 \pm 5.40\%$.
- Catalyst-free control reactions indicated that no hydrogen was produced via decomposition of the mediator.



OCCP measurements show:

- Rapid oxidation steps when MoS₂ is added. These are greater for greater catalyst loadings.
- A slower oxidation step showing a Nernstian curve profile is what follows until complete discharge. The slopes of these curves increase for greater amounts of catalyst. With 10 mg MoS₂, the Nernstian profile becomes much harder to observe.



UV-vis measurements show:

- Fresh purple CrPDTA solution exhibits two strong absorption peaks at 510 and 386 nm.
- Charged green CrPDTA does not display absorbance (low absorbance above 400 nm and high absorbance below 400 nm)
- Significant colour change for $t \geq 30$ s
- Complete discharge after 180 seconds.

5. Conclusion

- The **decoupled HER** can be carried out in **bicarbonate buffer** and in **near neutral pH**. Cr PDTA is a very negative redox couple that provides significant driving force for the HER. When paired with suitable catalysts, hydrogen evolves with very high faradaic efficiencies.
- The **highest faradaic yield** was obtained for **MoS₂** (93.39 ± 0.66), with the lowest being obtained for V10Pt ($60.29 \pm 5.40\%$). Changes in catalyst nanostructure, medium (pH, nature of the cation) may improve the faradaic efficiency values. Testing mediators with less negative potential may also improve electron transfer efficiency.
- Our work contributes towards the realisation of a **“dual circuit flow system”** operating in near neutral pH with suitable mediators for driving the reduction and oxidation reactions. These could produce hydrogen and valuable solid products on the oxidation side.



EIC Green Hydrogen Portfolio



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