

## Optimizing hydrogen evolution reaction on low-loaded Ru nanocatalysts supported on titanium oxynitride

<u>Milutin Smiljanić</u><sup>1</sup>, Marjan Bele<sup>1</sup>, Ivan Marić<sup>1,2</sup>, Luka Pavko<sup>1</sup>, Armin Hrnjić<sup>1</sup>, Francisco Ruiz-Zepeda<sup>1</sup>, Lazar Bijelić<sup>1</sup>, Aleš Marsel<sup>1</sup>, Lea Gašparič<sup>3</sup>, Anton Kokalj<sup>3</sup>, Nejc Hodnik<sup>1</sup>

Department of Materials Chemistry, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

<sup>2</sup>Division of Materials Chemistry, Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia

<sup>3</sup>Department of Physical and Organic Chemistry, Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia

Water electrolysis (WE) is anticipated to emerge as the leading technology for decentralized, carbon-neutral hydrogen production. In the WEs, hydrogen is generated through the electrochemical hydrogen evolution reaction (HER), and the effectiveness of catalysts for HER depends largely on the adsorption energy of hydrogen intermediates and the barrier for water dissociation. Refinement of these activity descriptors offers the potential to tailor advanced electrocatalysts beyond Pt, known for its superior HER performance.<sup>1</sup> Modern electrocatalysts are comprised of metallic nanoparticles as the active sites, backed on support materials, expected to provide effective anchoring, high surface area, and conductivity. In certain cases, support materials can also enhance the performance of active sites via metal-support interaction (MSI).<sup>2</sup>

This study showcases the effective HER catalyst comprising Ru supported on a titanium oxynitride—carbon template (Ru/TiON-C) with an exceptionally low Ru loading of 6 wt.%, Figure 1. In an alkaline electrolyte, the Ru/TiON-C composite exhibited superior HER activity compared to Ru/C and Pt/C (Figures 1a and 1b), ranking among the top-performing Ru-based catalysts documented in the literature. This enhancement was attributed to the ability of TiON to induce MSI with Ru, yielding two effects: (i) TiON prompted partial growth of a distorted fcc-Ru structure known for its enhanced water dissociation properties;<sup>3</sup> (ii) X-ray photoelectron spectroscopy suggested a rearrangement in the electron density of Ru-sites, which can lead to an adjustment of the hydrogen adsorption/desorption energy. Furthermore, Ru/TiON-C can be upgraded to obtain highly active catalysts for acidic HER by decorating it with only 2 wt.% Pt. The obtained RuPt/TiON-C catalyst matches the practical activity of a commercial Pt/C (20 wt.%) (Figure 1c) while significantly surpassing its mass activity.

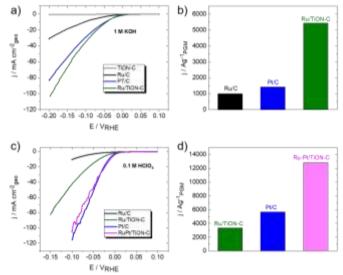


Figure 1. (a) Comparison of alkaline HER activities of Ru/C, Pt/C and Ru/TiON-C (1 M KOH, 10 mV/s) and (b) corresponding mass activities at an overpotential of 100 mV; (c) comparison of acidic HER activities of Ru/C, Ru/TiON-C, Pt/C and Pt-Ru/TiON-C catalysts (0.1 M HClO4, 10 mV/s) and (d) corresponding mass activities at an overpotential of 100 mV.

Acknowledgement: This work was financially supported by the Slovenian Research Agency through the research programs/projects P2-0393 and I0-0003 (OE 4), J7-4636, J7-4637, NC-0007, NC-0016, N2-0248, and N2-0155 and by European Research Council Starting Grant 123STABLE (Grant agreement ID: 852208).

## References

- 1. Hansen, J. N.; Prats, H.; Toudahl, K. K.; Mørch Secher, N.; Chan, K.; Kibsgaard, J.; Chorkendorff, I. Is There Anything Better than Pt for HER? ACS Energy Lett. (2021) 1175-1180 https://doi.org/10.1021/acsenergylett.1c00246
- Smiljanić, M.; Panić, S.; Bele, M.; Ruiz-Zepeda, F.; Pavko, L.; Gašparič, L.; Kokalj, A.; Gaberšček, M.; Hodnik, N. Improving the HER Activity and Stability of Pt Nanoparticles by Titanium Oxynitride Support. ACS Catal. 12(20) (2022) 13021-13033. https://doi.org/10.1021/acscatal.2c03214
- 3. Zheng, Y.; Jiao, Y.; Zhu, Y.; Li, L. H.; Han, Y.; Chen, Y.; Jaroniec, M.; Qiao, S. Z. High Electrocatalytic Hydrogen Evolution Activity of an Anomalous Ruthenium Catalyst. *J. Am. Chem. Soc.* **138(49)** (2016) 16174-161800. https://doi.org/10.1021/jacs.6b11291