Hydrogen post-treatment enhances the electrochemical activity of Pt-CeO₂/C catalysts

Huy Qui Vinh Nguyen^{1, *}, Heili Kasuk¹, Meelis Härmas¹, Jaan Aruväli², Olga Volobujeva³, Eneli Härk⁴, Zdravko Kochovski⁴, Enn Lust¹, Jaak Nerut¹

¹Institute of Chemistry, University of Tartu ²Institute of Ecology and Earth Sciences, University of Tartu ³Institute of Materials and Environmental Technology, Tallinn University of Technology ⁴Department of Electrochemical Energy Storage, Helmholtz-Zentrum Berlin für Materialien und Energie *vinh.nguyen@ut.ee

The Pt-CeO₂/C is one of the best catalyst candidates for proton exchange membrane direct methanol fuel cell $(DMFC)^1$, which converts the chemical energy of methanol to electric energy by electrochemical reactions in the catalyst layers. This type of device is suitable for long-range electric vehicles as the refuelling only takes few minutes. However, the low activity and degradation of catalyst layers prevent DMFC technology from being commercialised¹.

The Pt-CeO₂/C is a catalyst with good tolerance against the intermediate poisons from the methanol oxidation reaction (MOR) in DMFCs¹. However, the influence of CeO₂ particles with different sizes on the electrochemical activity of Pt-CeO₂/C catalyst has not been investigated. The gap in our understanding of the influence of CeO₂ particle size is crucial as CeO₂ impacts the electrochemical activity of Pt-based catalysts. Besides, according to the X-ray photoelectron spectroscopy results by Lu *et al.*², the presence of CeO₂ particles increases the ratio of Pt in higher oxidation state in the Pt-CeO₂/C catalyst. Therefore, the electrochemical activity of Pt-CeO₂/C catalyst synthesised by Lu *et al.* was enhanced because of that. However, in the previous study by Scibioh *et al.*³, the electrocatalytic activity of Pt-CeO₂/C was enhanced due to the higher Pt⁰ proportion. This conflict leads us to the question whether the thermal treatment using hydrogen gas can increase the Pt⁰ proportion, and therefore, improve the electrochemical activity of the Pt-CeO₂/C catalyst.

This study undertook the synthesis and characterisation of the Pt-CeO₂/C and Pt-CePO₄/C catalysts, both containing CeO₂ and CePO₄ compounds with diverse particle size (ranging from 3 nm to 0.8 μ m). The success of the synthesis of Pt-CeO₂/C particles with various sizes was confirmed by X-ray diffraction, scanning and transmission electron microscopy. The thermal treatment with the hydrogen gas was conducted for these materials. The electrochemical activity for MOR was evaluated using cyclic voltammetry and chronoamperometry (CA) measured in the mixture of 0.5 M H₂SO₄ and 1 M CH₃OH.

The hydrogen post-treatment was found to significantly alter the structure of Pt-CeO₂/C and Pt-CePO₄/C catalysts. The MOR electrochemical activity and durability of the Pt-CeO₂/C material containing 0.8 μ m CeO₂ particles were enhanced after the hydrogen post-treatment, while the MOR activity and durability at the Pt-CePO₄/C were dramatically reduced. There was no significant influence of hydrogen post-treatment on the MOR activity of the Pt-CeO₂/C catalysts containing 3 nm CeO₂ particles. The MOR activity of the Pt-CeO₂/C and Pt-CePO₄/C catalysts at the end of the CA at 0.85 V vs RHE was stable and was as high as 200 A g_{Pt}⁻¹. These results for MOR activity are as high as for other state of art Pt-CeO₂/C materials⁴.

Acknowledgements

This work was supported by the Estonian Research Council (Proof-of-Concept Grant EAG273), by the project "Increasing the knowledge intensity of Ida-Viru entrepreneurship" co-funded by the European Union (ÕÜF1), and by the Estonian Ministry of Education and Research (Center of Excellence TK210).

References

1 H. R. Corti and E. R. Gonzalez, Direct Alcohol Fuel Cells, Springer Netherlands, Dordrecht, 2014.

- 2 Q. Lu, Z. Wang, Y. Tang, C. Huang, A. Zhang, F. Liu, X. Liu, B. Shan and R. Chen, *Sustain. Energy Fuels*, 2022, 6, 2989–2995.
- 3 M. A. Scibioh, S.-K. Kim, E. A. Cho, T.-H. Lim, S.-A. Hong and H. Y. Ha, *Appl. Catal. B: Environ.*, 2008, **84**, 773–782.
- 4 S. Dai, J. Zhang, Y. Fu and W. Li, New J. Chem., 2018, 42, 18159–18165.