Electrocatalytic Activity of NH4⁺, Co²⁺ and Fe²⁺- doped MnO₂ as Cathode Catalysts in NH₃-based Fuel Cells

Luiza Zudina^{*1}, Anna K. Mechler¹, Georgii Sokolsky²

¹ RWTH Aachen University, Electrochemical Reaction Engineering (AVT.ERT), Germany ² National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Kyiv, Ukraine *E-mail: Luiza.Zudina@avt.rwth-aachen.de

Manganese oxides are widely applied in batteries as cathode material, where it is used as an active oxygen reduction reaction (ORR) catalyst.¹ C–MnO₂ is an alternative catalyst in fuel cells.² Direct ammonia fuel cells (DAFCs) are an interesting technology use ammonia as a hydrogen-carrier molecule to provide electricity while only producing water and nitrogen, resulting in no direct pollution to the environment.³ Not only the direct reduction of NH₃ is a catalytically interesting task, but also the cathode reaction, *i.e.*, oxygen reduction, needs to be reconsidered regarding the possibility of cross-over of NH₃ or NH₄⁺ through the membrane. Thus, an active and NH₃ tolerant ORR catalyst need to be found.

Manganese(IV) oxides (MnO₂) have a large diversity in their structure behaviour. The variety of polymorphs and a strong dependence of (electrochemical) properties on the preparation methods have been established.^{4,5} For instance, the phase composition and structural defects have influence the MnO₂materials activity. In a previous work, we presented a method for modifying MnO₂ by electrolytic doping with other cations, i.e. NH_4^+ , Co^{2+} and Fe^{2+} , which influence the phase composition, morphology and hence also modify the catalytic properties.⁶

First investigations indicate that MnO_2 is affected by the presence of NH_4^+ -ions in the electrolyte. Some materials, for instance with a higher amount of Co^{2+} -doping, even seem to have an improved performance in NH_4^+ -containing electrolyte. We will show detailed RDE studies on different materials with and without the presence of NH_4^+ in the electrolyte to identify critical structural properties for the interaction with cross-over NH_3 in ammonia fuel cell cathodes.

References

- 1. G.V. Sokolsky, Y.I. Boldyrev, N.D. Ivanova, S.V. Ivanov, G.Y. Kolbasov, G. Lazzara, L.V. Zudina, N.V. Gayuk, S.V. Chivikov, Surface and Coatings Technology, 400 (2020).
- Lu, L., Xu, H., Shi, J. *et al.* Pt-supported C–MnO₂ as a catalyst for polymer electrolyte membrane fuel cells. J Appl Electrochem 48, 801–810 (2018).
- 3. O. Siddiqui, I. Dincer, Development and performance evaluation of a direct ammonia fuel cell stack, Chem. Eng. Sci. 200 (2019) 285–293.
- 4. A.F. Wells, Structural Inorganic Chemistry, Oxford University Press, Oxford (1984).
- 5. Handbook of Manganese Dioxide Battery Grade, Eds. D. Glover, B. Schumm, A. Kozawa, International Battery Material Association (IBA Incorporated), (1989).
- 6. L. Zudina, G. Sokolsky, V. Chumak, N. Haiuk, Materials Today: Proceedings, 62, 15 (2022).