Operando ATR-IR assisted mechanistic study of the electrocatalytic methanol oxidation over a platinum catalyst in acidic medium

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Abstract

The advantage of methanol as fuel lies in the high energy density (15.6 MJ/L) and the readily used infrastructure for transportation and storage.[1,2] Possessing the highest catalytic activity among all the pure metals and outstanding resistance against harsh reaction conditions that are typically used in industry, platinum is still one of the most important catalysts applied in direct methanol fuel cells (DMFCs).[3–5] However, oxidation of methanol to CO_2 ($CH_3OH + H_2O \rightarrow CO_2 + 6\ H^+ + 6\ e^-$) to fully release the energy cannot be achieved, rather intermediates like formate and CO are formed, which could poison the catalyst. The role of these intermediates remains disputable, and the limited understanding of the mechanism impedes the broader application of the catalyst. Therefore, studies regarding the mechanism of the methanol oxidation reaction (MOR) still need be carried out to uncover the performance-determining factors. The project aims to shed light on the reaction mechanism of the MOR over Pt in acidic media by means of *operando* attenuated total reflection infrared (ATR-IR) spectroscopy, which allows fast product identification similar to differential electrochemical mass spectrometry. Downstream HPLC is also to be applied for the quantitative analysis of the species involved in the effluent of the applied borehole ring electrode (BHE).
The ATR-IR spectrometer cell adopts an Otto configuration, which features approaching the working electrode (WE) perpendicular to the internal reflection unit (IRE) and forming a thin electrolyte layer at the interface. A z-approach micrometer screw allows the fine adjustment of the thin layer thickness. Furthermore, a three-microelectrode-assisted tilt-correction system is integrated in the spectrometer cell so that the WE moves parallelly relative to the IRE thus securing the homogeneity of the electrolyte in the thin layer. Moreover, to overcome the limited mass transport, a BHE connected to a peristaltic pump is adopted, which supplies the fresh electrolyte to the thin layer and simultaneously withdraws the reacted electrolyte from the center of the thin layer for HPLC analysis.
Though successful design of the spectrometer and application for the MOR in alkaline medium, some challenges still remain such as the instable condition in the spectrometer cell in acidic medium impeding the acquisition of reproducible and high-quality spectra.

[1] F. Schorn, J. L. Breuer, R. C. Samsun, T. Schnorbus, B. Heuser, R. Peters, D. Stolten, *Advances in Applied Energy* **2021**, *3*, 100050.
[2] S. Sarp, S. Gonzalez Hernandez, C. Chen, S. W. Sheehan, *Joule* **2021**, *5*, 59.
[3] A. Kloke, F. von Stetten, R. Zengerle, S. Kerzenmacher, *Adv. Mater.* **2011**, *23*, 4976.
[4] H. Tian, Y. Yu, Q. Wang, J. Li, P. Rao, R. Li, Y. Du, C. Jia, J. Luo, P. Deng et al., *Int. J. Hydrog. Energy* **2021**, *46*, 31202.
[5] P. C. Meenu, S. Roy, C. Chakraborty, S. Roy, *Adv Powder Technol* **2021**, *32*, 2663