Mathematical model of non-equilibrium cathodic Pt dissolution

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Transformation of chemical energy, stored in hydrogen molecules, into electric energy using hydrogen fuel cells is an important building block of future green energy transition. Wider adoption of these devices is, however, still hindered by their relatively high cost and relatively high degradation rates due to harsh conditions inside the fuel cells.

An important reason for the high cost of proton exchange membrane fuel cells (PEMFCs) is utilization of expensive materials, such as Pt, which serves as a catalyst for electrochemical reactions. Despite its high resistivity to corrosion, high electric potential, temperature, and acidity in the fuel cell catalyst layer result in oxidation of Pt surface and its eventual dissolution, which severely limits the lifetime of PEMFCs. Experimental studies show that this process is further accelerated in dynamic conditions with periodically changing electric potential. When potential is increasing, Pt dissolution is suppressed by the formation of passive oxide layer, but when potential is subsequently lowered, the reduction of oxide layer results in severely increased concentration of dissolved Pt ions [1].

To improve the understanding of this process and its predictability, we propose a mathematical model of Pt surface oxidation, reduction, and dissolution. Pt oxidation at high electric potential is described as a two-step process, modelled by Butler-Volmer equations, with stable PtO oxide forming in the first step and subsequently, when the oxide surface coverage is increased, transforming into less stable α-PtO2 [2]. When the electric potential is subsequently decreased, instead of being reduced to Pt, part of α-PtO2 layer is detached from the surface, resulting in increased concentration of dissolved Pt ions in the adjacent electrolyte. The model is validated by comparing the results with experimentally measured time traces of Pt ion concentrations, determined with online ICP-MS, and with CV voltammograms, obtained during voltage cycling catalyst degradation test. Good agreement with experimental data indicates that the model meaningfully describes essential steps leading to increased Pt dissolution during the cathodic sweep of catalyst degradation. Due to its intuitive basis and computational efficiency, the model could, in future, be implemented in more complex model frameworks of fuel cell degradation, leading to development of advanced fuel cell operation strategies aimed at increasing their performance and lifetime [3].

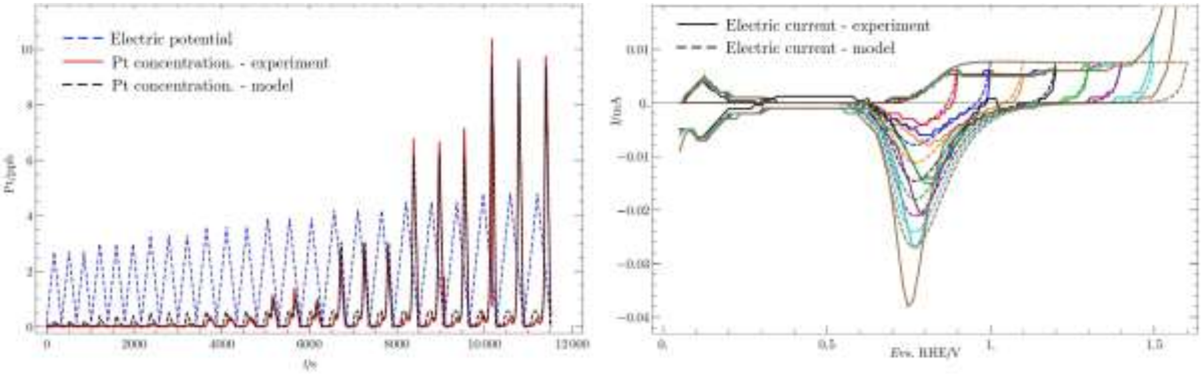

Figure 1. Comparison between experimentally measured and modeled Pt concentration and CV voltammograms

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References

1. A. Pavlišič, P. Jovanovič, V. S. Šelih, M. Šala, N. Hodnik, M. Gaberšček, *JES* **165(6)** (2018) F3161 https://doi.org/10.1149/2.0191806jes.
2. H. A. Baroody, G. Jerkiewicz, M. H. Eikerling, *J. Chem. Phys.* **146** (2017) 144102 https://doi.org/10.1063/1.4979121.
3. A. Kregar, M. Gatalo, N. Maselj, N. Hodnik, T. Katrašnik, *J. Power Sources* **514** (2021) 230542 https://doi.org/10.1016/j.jpowsour.2021.230542.