Electrochemical pressure impedance spectroscopy (EPIS) for investigation of transport phenomena in fuel cells

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Performance of polymer electrolyte fuel cells can be hindered by mass transfer control. For such cells with transport/transfer phenomena of reacting gases and liquid water, identification of the exact rate-determining transport phenomena by conventional techniques e.g. electrochemical impedance spectroscopy, is hardly possible. However, considering the gas pressure as an excitation variable and monitoring voltage fluctuations at constant current (EPIS) had shown promising [1-3] in experiments conducted in a fully instrumented test bench. Because of the "mechanical" input variable considered (here the outlet pressure of the cathode) and the tools used for its control and monitoring, the frequency range was restricted to 1 mHz – 1 Hz. Because of the very different diffusivity and viscosity of species in gas and in liquids, the range considered was expected suitable for observation of diffusion and convection of gases, water transport through the membrane. Also have to be considered in the analysis the hindering effect of liquid water in the channels or in gas diffusion layers on gas diffusion/convection. In any cases, signature of hindrance by transport phenomena could be observed on both the amplitude and phase shift of $Z_{V/P}$ (in V/Pa) in the whole frequency range.

With respect to gas phase transport, control by gas convection and oxygen diffusion in diluting nitrogen can be evidenced by the voltage-over-pressure impedance at frequencies larger than 30 mHz, with a flat peak of its modulus near 500 mHz and a regularly decreasing phase shift down from 0° at 1 Hz to approx. -180° at 1 Hz [3]. Liquid water formed upon increased humidity in the fuel cell gases was shown to dramatically increase the impedance modulus in the 0.1 – 1 Hz range, whereas the phase was not changed in a significant manner. The effect of gas convection is hardly visible par EPIS: this can be explained by the fact that the fuel cell performance – in terms of cell voltage at fixed current – is not directly affected by the intensity of its transport phenomenon.

The frequency domain (1-30 mHz) was also examined in experimental and theoretical works on water transport in the fuel cell, more particularly in the membrane. $Z_{V/P}$ below 30 mHz with a nil or moderate amount of liquid water in the fuel cell structure was measured as little significant, with a very restricted phase shift in this domain. EPIS impedance was shown to be mainly the fact of the dependence of the pressure Nernst contribution on the cell voltage, with restricted contribution from water dynamics in the membrane. Besides, in severe flooding conditions, fair EPIS signals with positive phase shifts up to +150° were observed.

[1] D. Grübl et al., J. Electrochem. Soc. 163, A599-A610 (2016)
[2] A.V. Shirsath et al., Curr. Opinion in Electrochemistry 20 (2020) 82–87.
[3] A.V. Shirsath et al., J. Power Sources, 531 (2022) 231341.

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