

In situ degradation measurements of a DMFC by a dynamic hydrogen reference electrode

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Direct methanol fuel cells (DMFC) are promising candidates for the low-power energy conversion sector. However, commercialization is still hindered due to several technical challenges such as slow electrokinetics of methanol oxidation (MOR) and oxygen reduction reaction (ORR) as well as methanol crossover [1]. As a result, high noble metal loadings are necessary leading to increased costs. The degradation phenomena can be classified in the following order with increasing significance: thermal, mechanical and chemical ageing. The latter is both caused by degradation of the carbon support and different catalyst ageing mechanisms. The precious metal catalysts may migrate and coalesce, dissolve and redeposit (electrochemical Ostwald ripening) or precipitate in the membrane [2]. DMFC ageing is even more severe since ruthenium in the bimetallic anode preferentially dissolves, which eventually leads to poisoning of the remaining platinum by intermediate methanol oxidation species.

In order to determine the individual contributions of the half-cells during long-term operation we have implemented a dynamic hydrogen reference electrode to measure the anodic and the cathodic potentials in situ. Here, two platinum wires are fixed on each side of the fuel cell, whereas a constant voltage sources is used to generate hydrogen and oxygen permanently at a low current [3]. The potentials are measured versus the hydrogen evolving wire which acts as dynamic reference electrode. This setup ensures an undisturbed operation of the fuel cell without further system modifications. The proof of principle for this method can be seen in Fig. 1. It is obvious that the anodic MOR occurs in a potential range from 200 to 600 mV vs. DHE whereas the cathodic ORR takes place in the range from 900 to 700 mV vs. DHE. Furthermore, measured total cell voltages and the differences of the half-cell potentials are in good agreement.

As an example for different employed ageing strategies, Figs. 2 and 3 show results obtained during operation at a constant current density ( $120 \text{ mA cm}^{-2}$ ) for approximately 200 h with interruptions after every 50 h, where electrochemical impedance spectra were taken. It can be seen that the anodic polarization strongly increases from initial 445 to 530 mV vs. DHE, whereas the cathodic polarization mainly remains unaltered. This indicates that the anode ageing is the major contribution to the performance loss of the fuel cell from initially  $42$  to about  $30 \text{ mW cm}^{-2}$ . EDX measurements of the aged membrane electrode assembly reveal a loss of ruthenium in the anode whereas an accumulation on the cathode was not found. It is also obvious that the DMFC performance is significantly improved directly after the impedance measurements at very low power density. This offers the opportunity to reduce ageing by regular current interruptions. In conclusion, we have shown that a dynamic hydrogen reference electrode is a valuable tool for in situ DMFC degradation measurements.

[1] G. Hoogers, Fuel Cell Technology Handbook, CRC Press LLC, 2003

[2] Büchi, F., Inaba, M. Schmidt, T., Polymer Electrolyte Fuel Cell Durability, Springer, 2009.

[3] Li, G. C., Pickup, P. G., 2004, Electrochimica Acta, 24, 4119-4126.

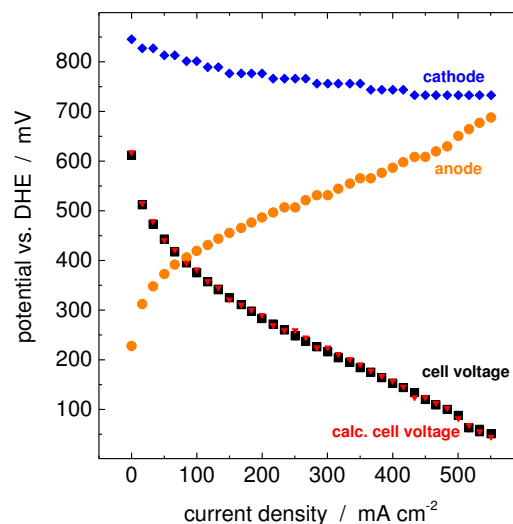


Fig. 1: Proof of principle of a dynamic hydrogen reference electrode

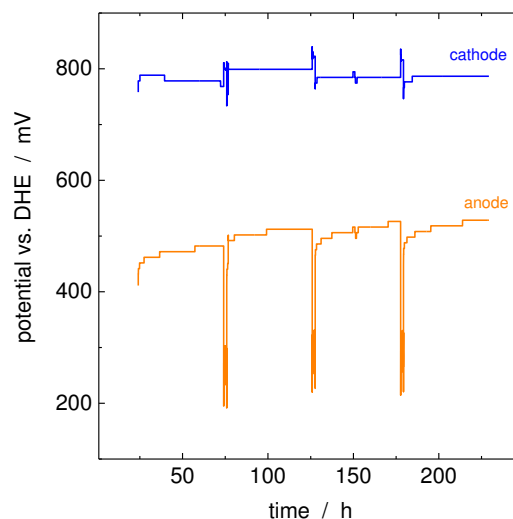


Fig. 2: Ageing curves of the anode and cathode vs. DHE, cell area:  $4.4 \text{ cm}^2$ ,  $1 \text{ mol L}^{-1}$  MeOH,  $5 \text{ mL min}^{-1}$  at anode,  $200 \text{ mL min}^{-1}$  pure oxygen at cathode,  $80 \text{ }^\circ\text{C}$ , operation at  $90 \text{ mA cm}^{-2}$

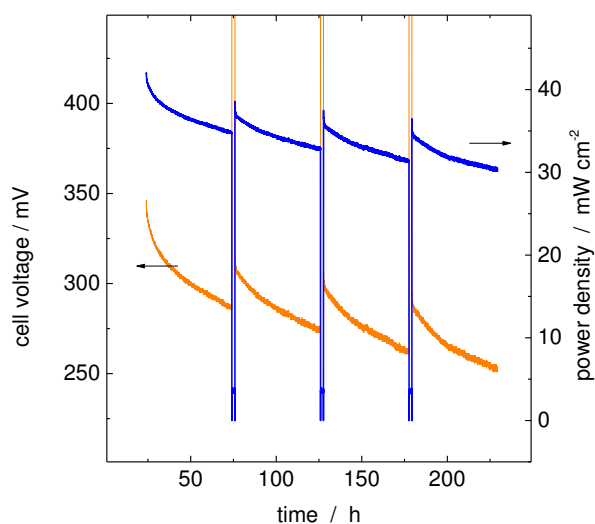


Fig. 3: Corresponding voltage and power density decay during long term operation at  $120 \text{ mA cm}^{-2}$