Proton Transport in Catalyst Layers of a Polymer Electrolyte Water Electrolyzer: Effect of the Anode Catalyst Loading

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The understanding of loss terms in polymer electrolyte water electrolysis (PEWE) cells is essential to maximize efficiency and minimize cost and enable the technology for energy applications, such as “power-to-X”. We adapt the use of the transmission-line model for porous electrodes in conjunction with electrochemical impedance spectroscopy measurements of the cell in the H₂/N₂ mode known for fuel cells to PEWE cells to quantify proton transport resistance and double layer capacitance of the anode catalyst layer. Anode catalyst loading was varied between 0.05 and 3.2 mg_{IrO₂} cm^{−2}. A non-linear relationship was found between the anode IrO₂ loading and the proton transport resistance. Catalyst layers with very low IrO₂ loading (0.05–0.16 mg_{IrO₂} cm^{−2}) had ~4 times higher mass-specific activity and ~2 times higher mass-specific capacitance, revealing an inhomogeneous utilization of the catalytic material. The kinetic and transport limitations associated with the anode catalyst layer have been correlated with its morphological features.

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Manuscript submitted September 4, 2018; revised manuscript received January 24, 2019. Published February 22, 2019.

The dynamic capabilities and wide current density operation range of polymer electrolyte water electrolysis (PEWE) make it attractive for converting renewable electricity from the grid to H₂ in the context of “power-to-X”.^{1–6} PEWE is especially attractive in power grids with a high share of fluctuating renewables, where the H₂ can be used for seasonal energy storage. H₂ as an energy vector is versatile since it can be re-electrified in a fuel cell for grid balancing, used in the mobility sector in fuel cell electric vehicles, or utilized in chemical industries to promote deep decarbonization of the energy sector.^{1,5} Furthermore, produced H₂ can be used in a downstream methanation process to form synthetic natural gas (SNG) using suitable, preferably renewable CO₂ and to feed it into the existing gas grid.⁶ Moreover, mixtures of H₂ and CO₂ can be used to produce syngas and subsequently liquid hydrocarbon energy carriers via a gas-to-liquid process.

The PEWE technology is currently plagued by issues associated with cost and component durability.^{7,8} The oxygen evolution reaction (OER) in acidic medium on the anode is currently catalyzed by precious materials from the platinum group metals (PGM). However, the cost of the catalyst materials has been estimated to contribute only 8% to the cost of the commercial stack.⁹ The final cost of the produced H₂ is not greatly affected by the cost contribution of the stack components.¹⁰ It is dominated by the cost of electricity (currently ~70% of the hydrogen end cost), and is therefore heavily dependent on the voltage efficiency of the stack.¹⁰ The type of the OER catalyst and its loading on the other hand have a large impact the stack voltage efficiency through the activation overpotential (η_{act}).^{11,12}

Iridium oxide (IrO₂) is the state-of-the-art PGM to catalyze the OER in commercial PEWE stacks.^{7,8} The most active material toward the OER is ruthenium oxide, but the dissolution rates remain too high for commercial implementation in the aggressive PEWE anode environment, in spite of extensive efforts to stabilize it.¹³ Higher loadings are preferred to maintain high stack voltage efficiency and reduce the end cost of H₂. Maintaining a high IrO₂ loading in the anode catalyst layer (CL_a) at high market penetration of PEWE in the energy sector might not be viable due to the low abundance and limited supply of iridium, especially considering it is a by-product of the Cu, Ni and Pt mining.¹⁴ The state-of-the-art PEWE stacks (~4 W cm^{−2} and 2 mg_{IrO₂} cm^{−2}) would require around 500 kg_{IrO₂}/GW. This would allow for an annual rate of capacity increase of 2 GW/a, considering the annual production rate of iridium of 4 tons per annum and assuming a use of 25% of this for PEWE.⁸ Reduction of the IrO₂ loading using

supported,^{15–17} high surface area catalysts^{18–20} or a nanostructured thin film catalyst²¹ is necessary to enable higher penetration of PEWE. On the other hand, reduction of the IrO₂ loading is only justifiable while maintaining high voltage efficiency of the PEWE stack.

Understanding the factors that determine the catalyst utilization is necessary to direct the development of the next-generation catalyst layers for the electrochemical water splitting technology. A set of diagnostic tools is required to benchmark catalyst layer performance and make correlations between the morphology and the overpotential in the polarization characteristics of a PEWE cell. In this study we present a detailed methodology for obtaining the proton transport resistance (R_{CLa}^{H+}) and the double layer capacitance of the CL_a from electrochemical impedance spectra collected in the H₂/N₂ regime. The approach has been widely used in polymer electrolyte fuel cell (PEFC) technology²² and is adapted here for a PEWE cell. The impedance is analyzed using the transmission-line model (TLM)^{22–26} to establish a correlation between the physical characteristics of the CL_a and the transport properties. The method is then tested on catalyst layers with loading varied between 0.05 and 3.2 mg_{IrO₂} cm^{−2}. The analysis is accompanied by cell voltage breakdown analysis based on the Tafel model previously reported in PEWE and PEFC literature.^{27–31}

Experimental

Cell and test-station.—A test bench developed in-house, equipped with a SP-150 potentiostat and a VMP3B 80A booster from Biologic was used to perform experiments. MiliQ water was circulated at a flow rate of 400 mL min^{−1} from a heated gas-water separator through the anode PEWE cell compartment. A PEWE cell with an active area of 25 cm² with parallel flow fields was used to accommodate commercial T10 sintered-Ti porous transport layers (PTLs) from GKN. The electro-osmotically dragged water was discarded periodically from the cathodic gas-water separator. Cell housing, inlet and outlet temperatures were monitored during the experiments, and the average temperature was used to specify the operating temperature.

CCM preparation.—In-house prepared CCMs were based on the Nafion 117 (DuPont) perfluorosulfonic acid membrane. Nafion 117 sheets of 10 × 10 cm were immersed in a ~30 vol% HNO₃ (VWR Chemicals) solution at 80°C for 1 h to protonate the sulfonic acid groups and remove impurities. Boiling steps were repeated 4 times in MiliQ water to remove the acid from the membrane. Membranes were dried for 12 h before weighing, and afterwards mounted into a PEEK-based frame for spraying.

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Table I. Properties of the IrO₂/TiO₂ based catalyst layers for PEWE. The catalyst layer thickness (d_{CLa}) is obtained from the CCM cross-sections observed with SEM. The anode catalyst layer proton transport resistance ($R_{\text{CLa}}^{\text{H}^+}$) and the double layer capacitance (C_{DL}) values are extracted from the cell impedance measured in the H₂/N₂ regime at 60°C. Proton resistivity of the anode catalyst layer ($\rho_{\text{CLa}}^{\text{H}^+}$) was calculated from $R_{\text{CLa}}^{\text{H}^+}$ and d_{CLa} values. The tortuosity (τ) of the electrode was calculated using Equation 5. The Tafel slope (b) and the anode catalyst activity (i_a) are extrapolated from the iR-free polarization curves at 60°C. The mass specific quantities c_{DL}^{m} and i_a^{m} are obtained by normalizing the calculated values to the IrO₂ loading.

Loading (mgIrO ₂ cm ⁻²)	d_{CLa} (μm)	$R_{\text{CLa}}^{\text{H}^+}$ (mΩ cm ²)	C_{DL} (F)	c_{DL}^{m} (F g ⁻¹)	i_a^{**} (A)	i_a^{m} (A g ⁻¹)	b (mV/dec)	$\rho_{\text{CLa}}^{\text{H}^+}$ (Ω cm)	τ^*
0.05	1.0 ± 0.2	38.9	0.1	119	0.07	55	70 ± 2	1062 ± 12	23.7 ± 0.6
0.16	1.1 ± 0.1	6.2	0.5	115	0.14	46	57 ± 1	164 ± 4	4.6 ± 0.7
0.8	2.6 ± 0.8	10.3	1.1	54	0.27	16	54 ± 1	120 ± 8	3.4 ± 0.6
1.2	3.5 ± 0.6	4.4	1.4	45	0.33	12	54 ± 2	38 ± 7	1.1 ± 0.7
1.8	4.3 ± 0.5	25.6	1.8	40	0.65	15	55 ± 1	179 ± 6	5.1 ± 0.5
2.6	5.8 ± 0.3	27.6	3.9	60	0.85	15	56 ± 1	144 ± 6	4.1 ± 0.6
3.2	8.3 ± 0.4	35.7	4.4	55	1.32	20	55 ± 1	129 ± 5	3.7 ± 0.8

Uncertainties for the other calculated values are provided in Figures 4, 5, 8.

*Calculated from the EIS in the H₂/N₂ regime.

**Calculated from the iR-free polarization curve at 1.47 V.

The anode catalyst ink was prepared by mixing 0.85 mL isopropanol, 2.7 mL miliQ water and 2.54 mL Nafion Solution (Aldrich, 5 w% Nafion). The ink was sonicated for 15 minutes. 1 g of IrTiO₂ catalyst (Umicore, 66 mol% IrO₂ and 34 mol% TiO₂) was added to the solution and sonicated for additional 30 min. The ink was sprayed onto the membrane using an airbrush pencil (Conrad Electronics Airbrush Pistol HP-200). The CCMs were dried again for 12 h and subsequently weighed. The ink-spraying preparation method yielded anode loadings from 0.05 to 3.2 mgIrO₂ cm⁻². A gas diffusion electrode (Johnson Matthey ELE-0244-0542 with HiSpec 9100 Pt/C 0.4 mgPt/cm²) was used as the cathode. The CCMs were assembled in the wet state after immersion in miliQ water for 12 h before testing.

Experimental conditions.—Cells were conditioned at 60°C by cycling the current density between 1 and 2 A cm⁻² until stable performance and uniform temperatures in the system were achieved. Polarization curves were recorded galvanostatically, while measuring the cell impedance at 10 kHz at every current step. The measurements were repeated at 50, 60 and 70°C. PEWE cells were operated in the H₂/N₂ regime to measure the ionic resistance of the anode catalyst layer. A N₂-stream of 500 Nml min⁻¹ was injected into the working electrode (WE) water loop, while the reference/counter electrode (RE/CE) was supplied with humidified H₂ at 400 Nml min⁻¹. We ensured no faradaic current was measured before recording the electrochemical impedance spectrum (EIS). The impedance in H₂/N₂ mode was recorded from 10 kHz to 300 mHz potentiostatically at 1.0, 1.2 and 1.4 V. No faradaic current was observed at these potentials during the collection of the impedance spectra. Cyclic voltammograms (CVs) were measured in the potential range between 0 and 1.4 V vs. RHE at a sweep rate of 50 mV/s.

Results and Discussion

Morphological analysis.—Post-test CCM samples were cryogenically fractured in liquid nitrogen and analyzed using a Zeiss Supra VP55 scanning electron microscope, with an acceleration voltage of 5 kV. CCM cross-sections were previously sputter-coated with a ~7 nm Cr-layer for better electrical conductivity. CCM cross-sections were investigated using the scanning electron microscope (SEM) to determine the thickness of the CL_a with different loadings (Table I), which was found to increase with $2.15 \pm 0.13 \mu\text{m mgIrO}_2^{-1} \text{cm}^2$. An airbrush sprayed CL_a consists of catalytic agglomerates 100–400 nm in size, connected by an ionomer film (Figure 1). The structure contains pores (voids) with a wide size distribution (0.1–1.5 μm in diameter). The cross-section of the 0.05 mgIrO₂ cm⁻² anode shows only a few catalytic agglomerates. The anode surface images reveal how the catalytic agglomerates are interconnected laterally. Lower loaded anodes are less homogeneous in-plane, and the ionic network is more frequently dis-

rupted. The CL_a of the 0.05 mgIrO₂ cm⁻² anode is very thin, and the agglomerates are often disconnected. The surface catalytic agglomerates of the thick CL_a are ionically well interconnected through the ionomer covering the agglomerates underneath.

Transmission line model for porous electrodes.—The AC impedance response of the CL_a is analyzed using the one-dimensional transmission-line model (TLM), typically used for the characterization of porous electrodes in electrochemical applications, including PEFC CLs.^{22–26} According to the TLM, the CL consists of differential elements describing the proton transport resistance, double layer capacitance (C_{DL}) and charge transfer resistance (R_{CT}) (Figure 2). The TLM is often simplified by using an inert gas fed working electrode (WE), and a H₂-fed reference/counter electrode (RE/CE). When the potential is applied, the permeating H₂ from the RE/CE cell compartment is the reactant for the permeation-rate limited hydrogen oxidation reaction (HOR) on the WE. The measured DC current corresponds to the hydrogen crossover current, which varies with the membrane thickness,

Figure 1. Surface of the anode catalyst layers with a loading of a) 0.05 mgIrO₂ cm⁻² and c) 1.2 mgIrO₂ cm⁻² and their respective cross-sections b) and d), observed under the scanning electron microscope.

Figure 2. Equivalent circuit of the transmission line model for porous electrodes, consisting of differential elements describing the proton transport resistance in the catalyst layer $R_{CL}^{H+,I}$, double layer capacitance C_{DL} and the kinetic resistance related to the electrochemical reaction R_{CT} . In the H_2/N_2 regime, the impact of the kinetic resistances becomes negligible ($R_{CT} \rightarrow \infty$) due to the near-absence of the faradaic reaction on the electrode.

temperature, pressure and relative humidity conditions in the cell. The crossover current does not contribute to the total impedance, and the low charge-transfer resistance of the HOR and the HER reactions allows for the simplification of the CL_a equivalent circuit (Figure 2). The electrode-electrolyte interface in this case behaves as a simple capacitor, which simplifies the analysis of the impedance spectra, as the charge-transfer arc following the high-frequency 45° region toward low frequencies vanishes (Figure 3).^{22,23} Deviation from the capacitive behavior at low frequency could result from structural inhomogeneity of the electrode.³² Impedance spectra are recorded at 1.0, 1.2 and 1.4 V representing a potential region beyond the OER regime.³³

The absence of a faradaic reaction on the WE greatly simplifies the impedance analysis and the estimation of the TLM equivalent circuit elements describing $R_{CL}^{H+,I}$ and C_{DL} . The equation describing the impedance response of the CL_a ²² can therefore be simplified according to

$$Z(f) = HFR + \sqrt{\frac{R_{CL}^{H+,I}}{2\pi f C_{DL} j}} \coth \left(\sqrt{2\pi f C_{DL} j R_{CL}^{H+,I}} \right) \quad [1]$$

where j is the imaginary unit (the symbol ' i ' is used for current density). In the special case when the frequency (f) tends to zero, the WE impedance becomes

$$\lim_{f \rightarrow 0} Z(f) = \lim_{f \rightarrow 0} [Re(Z) + jIm(Z)] \approx \frac{R_{CL}^{H+,I}}{3} - \frac{j}{2\pi f C_{DL}} \quad [2]$$

The C_{DL} can be obtained from the limiting impedance at low f .²² Instead of assuming constant $Im(Z)$ and averaging it at low f ,²⁴ we have estimated the C_{DL} according to Equation 3 using $Im(Z)$ at the minimum phase angle (φ_{min}), when the transition to the capacitive behavior sets in. The φ_{min} is obtain at lower frequencies for thicker CL_a , as the AC current needs to penetrate longer pores. When the pores are penetrated, the φ goes through a minimum value and increases asymptotically to 90° . The uncertainty of averaging is in this way mitigated, since the $Im(Z)$ in Equation 2 often does not exhibit a plateau at low f , especially with low catalyst loadings.³⁴ Another way to calculate C_{DL} is by dividing the average CV current in the potential range of 1.0–1.4 V by the sweep rate. C_{DL} obtained from the CV appears to be higher compared to the C_{DL} calculated from the EIS in the H_2/N_2 regime. (Figure 4a). Higher C_{DL} measured in the CV can be related to the pseudocapacitance resulting from the fast electrosorption processes while cycling the electrode potential. For both methods C_{DL} increases with the anode loading due to the increase of the absolute catalyst mass and therefore the surface area.

The mass-specific capacitance (c_{DL}^m) normalized to the amount of IrO_2 in the active area shows little deviation between the anodes with different IrO_2 loading, except for the samples with 0.05 and 0.16 $mg_{IrO_2} cm^{-2}$ where it is approximately 2 times higher. Deviation from the constant c_{DL}^m could be related to the inhomogeneous utilization of the catalyst in the case of thicker CL_a with higher loading. A trend similar to the one of C_{DL} and c_{DL}^m vs. the IrO_2 loading is observed (cf. below) when estimating the mass-specific activity from the iR -free polarization curves. It is assumed that the TiO_2 in the catalyst layer is an insulator and that the electronic conductivity of the catalyst is ensured through the IrO_2 percolation network.³⁵ The capacitances are normalized only to the mass of IrO_2 , since the contribution of TiO_2 would in this case be negligible. At high f , the 45° region appears in the Nyquist plot (Figure 3). Here, the impedance can be described by

$$Z(f) \approx HFR + \sqrt{\frac{R_{CL}^{H+,I}}{2\pi f C_{DL} j}} \quad [3]$$

followed by the capacitive region at low frequencies, represented by the 90° line in the Nyquist plot and the HFR-corrected impedance

Figure 3. a) HFR-corrected impedance response of the PEWE cell with $0.8 mg_{IrO_2} cm^{-2}$ in the H_2/N_2 regime measured at 50, 60 and $70^\circ C$, showing the temperature dependence of $R_{CL}^{H+,I}$. Impedance of the cell with $3.2 mg_{IrO_2} cm^{-2}$ is included to demonstrate the increase of $R_{CL}^{H+,I}$ with the thickness of the anode catalyst layer. b) Bode phase plot of the cell with $0.8 mg_{IrO_2} cm^{-2}$ in the H_2/N_2 regime measured at 50, 60 and $70^\circ C$, and of the cell with $3.2 mg_{IrO_2} cm^{-2}$ at $60^\circ C$. The $R_{CL}^{H+,I}/3$ projection is obtained by first finding f_{min} at which φ_{min} appears in b), and extracting the impedance at f_{min} from the Nyquist plot in a).

Figure 4. a) Double layer capacitance C_{DL} and b) mass-specific capacitance c_{DL}^m of anode catalyst layers with different catalyst loading estimated from the cyclic voltammogram (red) and the impedance in the H_2/N_2 regime (black).

given by

$$Z(f) \approx \frac{R_{CLa}^{H+}}{3} + \frac{1}{jC_{DL}f} \quad [4]$$

$R_{CLa}^{H+}/3$ can be extracted from the Nyquist plots of H_2/N_2 operated cells by projecting the low f impedance vertically to the real axis (Figure 3).^{22,32,33} An alternative approach is to determine C_{DL} from Equation 3 and calculate R_{CLa}^{H+} .²⁴⁻²⁶ Graphical extrapolation of R_{CLa}^{H+} from the Nyquist plot relies on the presence of a vertical, capacitive impedance at low f , which is not always observed in the measured data.^{22,33,36} Deviations from the low f capacitive behavior can be attributed to inhomogeneity of the catalyst layer, stemming from the preparation process or caused by the coarse PTL surface.^{32,37} The morphologic properties of the CL together with the CL/PTL interface properties might result in electrically insulated regions in the CL with high resistance, accessible only at low f .³⁷ Furthermore, the wetting of the CL pores could be non-uniform in PEWE,^{11,33} resulting in distributed capacitance through the CL thickness. This can lead to a large variance in the extrapolation of the R_{CLa}^{H+} (Figure 5). On the other hand, approximation of C_{DL} from Equation 3 requires that $-\text{Im}(Z)$ plateaus at low f .²⁴ If this is not the case, the uncertainty in the calculation of C_{DL} , and subsequently of R_{CLa}^{H+} , increases. To circumvent the possible issues and errors in the estimation of C_{DL} , we propose a method of finding the C_{DL} values at the frequency at which a minimum in the phase angle φ is observed. This point marks the impedance transition from the 45° region to the capacitive behavior. HFR-corrected impedance spectra in H_2/N_2 mode are used to calculate the φ values (Figure 3), and the value of $f_{\varphi\min}$ is obtained at $\varphi_{\min}$. The method results in a defined knee-point in the Nyquist plot based on the pore length, from which R_{CLa}^{H+} and C_{DL} can be calculated. The $f_{\varphi\min}$ is lower for thicker catalyst layers since the current has to penetrate longer distances, which is evident in

Figure 5. Comparison of R_{CLa}^{H+} values calculated using the $f_{\varphi\min}$ approach (cf. Figure 3) and from the graphical extrapolation of the vertical line at low f . The minimum R_{CLa}^{H+} is observed for the sample with an IrO_2 loading in the range from 0.16 to $1.2 \text{ mg}_{\text{IrO}_2} \text{cm}^{-2}$.

Figure 3 for samples of 3.2 vs. $0.8 \text{ mg}_{\text{IrO}_2} \text{cm}^{-2}$. In this study we have used both methods and compared the R_{CLa}^{H+} values obtained for PEWE anodes with catalyst loading ranging from 0.05 to $3.2 \text{ mg}_{\text{IrO}_2} \text{cm}^{-2}$. The values of R_{CLa}^{H+} obtained from the graphical extrapolation from the Nyquist plot and from the C_{DL} at $f_{\varphi\min}$ are shown in Figure 5. Graphical extrapolation resulted in higher values of R_{CLa}^{H+} in the case of very low and very high loadings, while both methods yield similar R_{CLa}^{H+} for the cells with 1.8 and $2.6 \text{ mg}_{\text{IrO}_2} \text{cm}^{-2}$.

The measured R_{CLa}^{H+} decreases with higher cell temperatures due to the increased ionic conductivity of the ionomer in the CL_a ($13.0/10.3/9.1 \text{ m}\Omega \text{cm}^2$ at $50/60/70^\circ\text{C}$ for $0.8 \text{ mg}_{\text{IrO}_2} \text{cm}^{-2}$, respectively, based on data from Figure 3). The contribution of the ionic resistance of the CL_a appears as a loss term of magnitude $R_{CLa}^{H+}/3$ in the polarization curve, as part of mass transport losses (η_{mtx}).^{24,33,38} Improved proton transport in the CL_a would partially account for the temperature dependent η_{mtx} previously reported by Suermann et al.²⁸ The change of η_{mtx} at 1 A cm^{-2} between 50 and 70°C was $\sim 7 \text{ mV}$ for the CL with $0.8 \text{ mg}_{\text{IrO}_2} \text{cm}^{-2}$ in this study. The change in the area resistance of a $\sim 3 \mu\text{m}$ thick Nafion ionomer sheet between 50 and 70°C is in the range of $\sim 1 \text{ m}\Omega \text{cm}^2$ (measured value in the H_2/N_2 regime $\sim 4 \text{ m}\Omega \text{cm}^2$), and can only account for a fraction of $\Delta\eta_{\text{mtx}}$. Stronger sensitivity of R_{CLa}^{H+} to temperature variations during H_2/N_2 measurements compared to what is reported for Nafion³⁹ could stem from thin film limitations and the water distribution in the CL as a factor of the PTL/CL interface, and will be discussed further in the overpotential breakdown section below.

Considering CL_a as a sheet electrode, R_{CLa}^{H+} would decrease with the thickness, hence lower IrO_2 loading.²⁵ Two trends of R_{CLa}^{H+} have been observed with varying loading in the H_2/N_2 regime. R_{CLa}^{H+} decreases with decreasing loading in the range from 3.2 to $1.2 \text{ mg}_{\text{IrO}_2} \text{cm}^{-2}$ on the account of lower CL_a thickness, since the proton transport path is longer for thicker catalyst layers. The lowest R_{CLa}^{H+} values were observed for the IrO_2 loading range from 1.2 to $0.16 \text{ mg}_{\text{IrO}_2} \text{cm}^{-2}$. Interestingly, R_{CLa}^{H+} was highest for the sample with $0.05 \text{ mg}_{\text{IrO}_2} \text{cm}^{-2}$. Proton transport from the catalytically active sites relies both on through-plane as well as in-plane transport when the structure is composed of catalytic agglomerates connected by the ionomer. At very low IrO_2 loading applied using the airbrush method the CL_a structure becomes less homogeneous, as observed in the SEM images. This results in a

lower degree of connectivity between the catalyst agglomerates by the ionomer network and subsequently higher in-plane resistance contribution to the $R_{\text{CLa}}^{\text{H}+}$. Alternative catalyst structures, such as the nanostructured thin film catalyst (NSTF) developed by 3M,²¹ and different application methods⁴⁰ are necessary to achieve low-loaded anodes with uniform structure. The deviation of the measured impedance from the characteristic 45° slope at high f is more pronounced for the CL_a with low IrO₂ loading ($<1.2 \text{ mg IrO}_2 \text{ cm}^{-2}$). This behavior of the impedance has previously been ascribed to electrodes with open, wedge-shaped pores,^{41,42} which is the case for low-loaded anodes with inhomogeneous distribution and packing of the catalyst agglomerates. Other possible causes of non-linear behavior of $R_{\text{CLa}}^{\text{H}+}$ with varying IrO₂ loading are discussed in more detail in the section on overpotential analysis, in the context of the mass transport losses.

The average proton resistivity of the anode catalyst layers with $>0.05 \text{ mg IrO}_2 \text{ cm}^{-2}$ ($\rho_{\text{CLa}}^{\text{H}+}$) was found to be $130 \pm 33 \Omega \text{ cm}$, using the $R_{\text{CLa}}^{\text{H}+}$ and the CL_a thickness (d_{CLa}) values from the SEM cross-sectional images (Table I). The calculated value is in the range of values typically obtained for a fuel cell catalyst layer under fully humidified conditions at low ionomer to carbon ratio.²⁶ The reason for a large variation in $\rho_{\text{CLa}}^{\text{H}+}$ in the case of $0.05 \text{ mg IrO}_2 \text{ cm}^{-2}$ is the strong deviation of the calculated $R_{\text{CLa}}^{\text{H}+}$ from the decreasing trend with the IrO₂ loading. $\rho_{\text{CLa}}^{\text{H}+}$ is normally found to be a property of the catalyst layer that is independent of its thickness.²⁶ Our CL_a structure is laterally very inhomogeneous at lower loadings, and the corresponding in-plane $R_{\text{CLa}}^{\text{H}+}$ contribution results in an increase of the apparent $\rho_{\text{CLa}}^{\text{H}+}$. Taking the ionomer resistivity ($\rho_i^{\text{H}+}$) from the literature and using the ionomer volume fraction in the electrode (ε_i), the tortuosity (τ) can be calculated:

$$\tau(\varepsilon) = \frac{\rho_{\text{CLa}}^{\text{H}+} \varepsilon_i}{\rho_i} \quad [5]$$

We obtained $\varepsilon_i = 0.314$, following the equations given in detail by Liu et al.,²⁶ and assumed $\rho_i^{\text{H}+}$ from 8 to $11 \Omega \text{ cm}$ ^{26,43} to find that τ goes through a minimum close to 1 for the cell with a loading of $1.2 \text{ mg IrO}_2 \text{ cm}^{-2}$ (Table I). The findings from the H₂/N₂ measurements suggest that the ionomer does not form a well-connected network between the catalytic agglomerates especially in the case of $0.05 \text{ mg IrO}_2 \text{ cm}^{-2}$, which is reflected in the $R_{\text{CLa}}^{\text{H}+}$ and the η_{mtx} values in the overpotential analysis.

Overpotential breakdown.—The overpotential breakdown of the PEWE polarization curve was conducted according to the procedure described in the Appendix. Polarization curves of PEWE cells with differently loaded CL_a have been iR -corrected using the HFR to eliminate the influence of the variations in ohmic overpotential (η_{Ω}) that might stem from small variations in the cell assembly, membrane ionic resistance and contact resistances with different PTL samples. The HFR was found to be $257 \pm 16 \text{ m}\Omega \text{ cm}^2$ for all samples at 60°C , without any correlation to the IrO₂ loading. Increasing the CL_a loading results in lower $E_{iR\text{-free}}$ (Figure 6), which is lowest for the highest loading ($3.2 \text{ mg IrO}_2 \text{ cm}^{-2}$) and highest for the lowest loading ($0.05 \text{ mg IrO}_2 \text{ cm}^{-2}$), as may be expected. The $E_{iR\text{-free}}$ values of the cells with $0.16\text{--}3.2 \text{ mg IrO}_2 \text{ cm}^{-2}$ have a constant Tafel slope b of $55 \pm 1 \text{ mV/dec}$, and are offset by a factor depending on the CL_a loading. The Tafel slope is higher only in the case of the $0.05 \text{ mg IrO}_2 \text{ cm}^{-2}$ sample with 70 mV/dec . A similar effect of the CL_a loading on the Tafel slope was observed by Bernt et al.,¹¹ albeit already at $0.2 \text{ mg IrO}_2 \text{ cm}^{-2}$. The catalyst activity i_a , expressed as the current density at a fixed $E_{iR\text{-free}}$ of 1.47 V , increased linearly with the CL_a loading, as expected. The calculated mass activity i_a^m is in the range of $10.2 \pm 1.3 \text{ A g}^{-1}$ for the cells with CL_a loading between 0.8 and $3.2 \text{ mg IrO}_2 \text{ cm}^{-2}$. However, the i_a^m for the cell with $0.16 \text{ mg IrO}_2 \text{ cm}^{-2}$ is found to be approximately three times higher (Figure 7). Decreasing the loading even further to $0.05 \text{ mg IrO}_2 \text{ cm}^{-2}$ results in i_a^m of $54.8 \pm 4.2 \text{ A g}^{-1}$. The deviation of i_a^m in the case of CL_a with a very low IrO₂ loading ($<0.2 \text{ mg IrO}_2 \text{ cm}^{-2}$) indicates that the catalyst utilization of higher loaded CLs is low.⁴⁴ Operando optical imaging studies of the O₂ nucleation at the

Figure 6. $E_{iR\text{-free}}$, η_{act} and η_{mtx} for the cells with different IrO₂ loadings. Data were obtained by iR -correcting the polarization curves using the HFR at 10 kHz measured at 60°C and atmospheric pressure.

PTL/CL_a interface suggest that O₂ evolution is localized at the CL_a in direct contact with the PTL, while the catalyst in the PTL void (size: $50\text{--}500 \mu\text{m}$) remained inactive.^{45–48} The limiting factor toward optimal catalyst utilization was the insufficient electronic conductivity of the catalyst layer.^{11,44–48} Assuming negligible differences in the in- and through-plane electronic conductivity of the CL_a, the catalyst material

Figure 7. Activity in the form of the current measured at a fixed iR -free potential of 1.47 V (black), and the activity normalized to the IrO₂ loading (mass activity, red).

Figure 8. Schematic representation of the PEWE anode catalyst layer. The ionomer phase conducts protons from the catalytically active surface sites. The metallic phase provides the electronic conductivity of the layer.

closer to the PEM would not be fully utilized. Although more catalyst contributes to the OER in the case of anodes with higher IrO_2 loading, the fraction of active material would be lower. This effect is illustrated in Figure 8.

The variation of the IrO_2 loading affected η_{mtx} in a similar fashion as the $R_{\text{CLa}}^{\text{H}^+}$ obtained in H_2/N_2 configuration, i.e. in the absence of faradaic current (Figure 9). Since the $R_{\text{CLa}}^{\text{H}^+}$ contribution appears as a part of the η_{mtx} ,^{33,38} a good correlation in the trend of these two independently determined quantities can be taken as a validation of the transmission line model method to determine $R_{\text{CLa}}^{\text{H}^+}$ in PEWE cells. Structural inhomogeneity of low IrO_2 -loaded CL_a related to the preparation method could be the cause of the non-linear behavior of $R_{\text{CLa}}^{\text{H}^+}$, and consequently η_{mtx} . Low IrO_2 loadings were found to have a similar effect on the electronic conductivity of the catalyst layer.¹¹ It is important to note that $R_{\text{CLa}}^{\text{H}^+}$ is very sensitive to variations in the water content of the ionomer in the CL_a .^{22,24–26} Bernt et al.¹¹ have suggested that the water distribution might be different for thick and thin CL_a ,

Figure 9. $R_{\text{CLa}}^{\text{H}^+}/3$ (red) and η_{mtx} (black) at 1 (■), 2 (●) and 3 (▲) A cm^{-2} for anode catalyst layers with different IrO_2 loading, 60°C.

which would affect $R_{\text{CLa}}^{\text{H}^+}$, and ultimately η_{mtx} . As the OER in PEWE cells occurs below the PTL particles,^{45–48} the water has to diffuse both laterally and perpendicularly to the membrane surface (Figure 8) from the PTL pore to the active sites below the PTL particle.³³ Since the water diffusion through Nafion thin films ($< 60 \text{ nm}$) is orders of magnitude slower compared to the bulk,^{49,50} thicker CLs would result in longer diffusion distances for the reactant, and thus yield an inhomogeneous water distribution in the CL. Development of an anodic PTL with a microporous layer is necessary to alleviate problems which diminish the electronic and ionic connectivity of anode CLs with low IrO_2 loadings.¹¹

Conclusions

Understanding the relationship between cell performance and the structural features of the anode catalyst layer in PEWE is necessary for tailoring next-generation catalyst layers for optimal transport properties and activity. We provide a methodology to determine the proton transport resistance in the anode catalyst layer, $R_{\text{CLa}}^{\text{H}^+}$, based on impedance measurements in the H_2/N_2 regime by identifying the knee point in the Nyquist plot corresponding to the minimum phase angle observed in the Bode phase plot. The presented diagnostic method is a universal tool for characterizing catalyst layers for water electrolyzers. Application of the method to anodes with varying IrO_2 loading from 0.05 to 3.2 $\text{mg}_{\text{IrO}_2} \text{ cm}^{-2}$ has revealed that the loading affects $R_{\text{CLa}}^{\text{H}^+}$ in a non-linear fashion. Overpotential analysis showed that there is a correlation between the trends observed in $R_{\text{CLa}}^{\text{H}^+}$ and the mass transport overpotential η_{mtx} versus the IrO_2 loading. Low loaded anodes ($< 1.2 \text{ mg}_{\text{IrO}_2} \text{ cm}^{-2}$) exhibit a high degree of in-plane inhomogeneity, which could explain the non-linear relation between the IrO_2 loading and $R_{\text{CLa}}^{\text{H}^+}$. Other potential causes related to the water management in the catalyst layer are discussed in the context of η_{mtx} values measured with different IrO_2 loadings.

We have demonstrated that more IrO_2 catalyst yields lower activation losses, as expected, yet a lower effective utilization of the material. Moreover, a systematic variation of the IrO_2 loading has revealed a relationship between the activation overpotential η_{act} and η_{mtx} that can to a certain extent compensate the apparent loss of voltage efficiency in going toward lower IrO_2 loading. Optimizing the morphology of the catalyst layer by adapting the preparation method could open a pathway to low loaded catalyst layers with high volumetric utilization of the active material.

Acknowledgments

Funding by the Swiss Federal Office of Energy (grant-no. 501198-01) is gratefully acknowledged. TJS thanks Innosuisse and the Swiss Competence Center for Energy Research Heat & Electricity Storage. We acknowledge Katrine Elsoe (DTU) for performing preliminary series of catalyst layer coating trials in the framework of a research stay at PSI.

Appendix

Overpotential analysis.—The electrolyzer cell voltage (E_{cell}) is composed of the reversible cell voltage (E_{rev}), ohmic (η_{Ω}), kinetic (η_{act}), and mass-transport (η_{mtx}) overpotentials (Equation A1).^{27–29,33}

$$E_{\text{cell}} = E_{\text{rev}} + \eta_{\text{act}} + \eta_{\Omega} + \eta_{\text{mtx}} = E_{\text{rev}} + \eta_{\text{act}} + i \cdot (R_{\text{PEM}} + R_{\text{el}}) + i \cdot R_{\text{CLa}}^{\text{H}^+} + \eta_{\text{mtx-rest}} \quad [\text{A1}]$$

E_{rev} is given by the Nernst equation for the operating pressure, temperature and the activity of the species involved in the reaction (Equation A2). We assume unity for the activity of water and ideal gas behavior for the gases. For the temperatures used in this study, 50°C, 60°C, 70°C, E_{rev} is 1.195 V, 1.186 V, 1.177 V, respectively.

$$E_{\text{rev}}(p, T) = E_{\text{rev}}^0(T) + \frac{R \cdot T}{2 \cdot F} \ln \left(\frac{a(\text{H}_2) \cdot \sqrt{a(\text{O}_2)}}{a(\text{H}_2\text{O})} \right) \quad [\text{A2}]$$

η_{ohm} is the result of losses related to the membrane proton transport processes (R_{PEM}) and the contact resistances (R_{el}) and follows Ohm's law, $\eta_{\Omega} = i \cdot (R_{\text{PEM}} + R_{\text{el}})$.^{7,51} These losses are obtained when correcting the polarization curve with the high-frequency resistance (HFR), in this case measured at 10 kHz. η_{act} is related to sustaining the sluggish anodic

oxygen evolution reaction (OER).⁵² The cathode reaction is assumed not to be kinetically limiting.³⁸ η_{act} is obtained by subtracting E_{rev} from the Tafel line, which is calculated from the iR -free cell voltage ($E_{iR-\text{free}}$) at low current densities ($0.01\text{--}0.1\text{ A cm}^{-2}$). η_{mix} appears at higher current densities and is obtained from the difference of $E_{iR-\text{free}}$ and the fitted Tafel line. Part of η_{mix} is related to the proton transport resistance in the CL_a,^{11,33,38} and can be obtained from the Nyquist plot of the EIS during H₂/N₂ operation.³³

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