CO₂-Assisted Regeneration of a Polymer Electrolyte Water Electrolyzer Contaminated with Metal Ion Impurities

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Polymer electrolyte water electrolysis (PEWE) is perceived as a key technology for conversion of renewable electricity in large-scale energy storage applications and deep decarbonization of the traditionally carbon-intensive mobility and chemical industry sectors. Since the price of hydrogen produced by PEWE is dominated by the price of electricity, it is crucial to ensure low degradation rates during the lifetime of a PEWE stack. This study aims to shed light onto the effects of cationic impurities that are responsible for the water impurity related failures of a majority of commercial stacks by employing operando neutron imaging coupled with electrochemical impedance spectroscopy measurements. A detailed overpotential analysis is conducted to elucidate how different voltage losses are triggered depending on the relative position of the cationic contaminant in the catalyst coated membrane. Based on this, a novel, CO₂ – assisted, method for the extraction of cationic impurities from the ionomer of the electrolyzer to recover performance during operation of the cell is presented.

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Polymer electrolyte water electrolysis (PEWE) is perceived as a key technology for coupling different sectors in future sustainable energy scenarios in the Power-to-X framework.^{1,2} Large amounts of excess electricity can be stored via the electrochemical water splitting in the form of chemical energy. The produced H₂ is a versatile energy vector and can be utilized in fuel cell electric vehicles to promote deep decarbonization of the energy economy. Furthermore, H₂ can be used to methanate CO₂ from renewable sources (e.g., bio-waste) to produce synthetic natural gas, which can directly be stored in the natural gas grid (Power-to-Gas), or converted to liquid hydrocarbon energy carriers (Gas-to-Liquid). Last but not least, an important market readily exists for H₂, in particular in the chemical industry, e.g., for the production of fertilizers. The use of H₂ from renewable sources in this market represents an important potential for the reduction of CO₂ emissions, as the current H₂ production is mostly based on fossil fuels.^{3–8}

Much of the research effort in the PEWE is targeted at improving the stack voltage efficiency through material and component innovation. Novel porous transport layers (PTLs) receive considerable R&D attention to minimize the losses associated with the two-phase flow and the interface to the catalyst layer (CL).^{9–16} Innovation in the field of electrocatalysis is focused on developing high surface area,^{17–20} supported^{21–23} catalyst, and novel CL preparation methods.²⁴ Membrane development is targeting thin membranes with improved gas barrier and mechanical properties to reduce the ohmic overpotential while maintaining high faradaic efficiency.^{25–27}

Since the end-cost of the produced H₂ is dominated by the electricity cost,²⁸ increasing the stack voltage efficiency is necessary to ensure that PEWE can prosper in the energy market as one of its future backbone technologies. In this context, it is crucial to maintain high stack voltage efficiency during the lifetime of the PEWE. Currently, commercial stacks are envisioned to operate up to 90,000 h.²⁹ Studies and industry reports dealing with degradation of commercial PEWE components report that the most common failure mechanism in field operation is the reversible contamination by the impurities in the feed-water.^{30–32} Cationic impurities (Ca²⁺, Cu²⁺, Ni²⁺, Pb²⁺, Fe³⁺, Ti²⁺) may be present in the anodic feed water as a result of corrosion of system components or user contamination.^{31–35} Cationic impurities migrate through the ionomer of the catalyst coated membrane (CCM) under the influence of the electric field and occupy ion-exchange sites,

reducing proton conductivity in the ionomer,^{31,32,36} which results in increased cathodic and anodic overpotentials³³ due to additional ohmic losses.³² Moreover, Fenton active transition metal ions (Ni, Fe, Cu) can promote chemical degradation of the polymer backbone by catalyzing the formation of radicals (OH[•], H[•]).³⁷ The emission of metallic cations from PEWE system components can be suppressed by coating the relevant parts with protective metal coatings.^{31,38,39} Furthermore, an ion exchange resin can be incorporated into the feed water loop to scavenge ionic species. The contamination of the ionomer by foreign cations is reversible by protonating the ionomer using an acidic medium (H₂SO₄(aq), HNO₃(aq), etc.) through ion-exchange.³² This is often done by disassembly of the stack and immersion of the CCM in aqueous sulphuric acid, or by introducing an acid to the feed water loop of the electrolyzer.^{40,41} The latter could, however, result in corrosion of unprotected system metal components. An ion exchange process between the contaminant in the CCM and protons can be triggered by lowering the pH of the anodic and cathodic water loops via pressurized CO₂ gas and the subsequent formation of H₂CO₃. A pH as low as 3.0 could be achieved at 20°C and a pressure of 50 bar_a.⁴² Depressurization of the feed water loop would result in restored neutral pH.

The study presented here focuses on the effects of the contaminant in the CCM on the voltage losses of a PEWE cell. In addition, a novel operando regeneration strategy is presented to restore the performance of a cationically contaminated cell. Two sets of experiments are conducted to tackle this issue. A first type of experiment was conducted using Gd³⁺ contaminant during operando neutron imaging in order to track the location of the contaminant in the CCM during electrolyzer operation. Gd³⁺ was selected due to its high contrast versus other cell materials in neutron radiograms, resulting from its high neutron attenuation coefficient.⁴³ A second set of experiments was performed using the more common Fe³⁺ contaminant, and electrochemical impedance spectroscopy was used to conduct a detailed overpotential breakdown in order to track the change in ohmic, activation and mass transport contribution to the performance decay during the contamination phase. Iron is a common contaminant from steel-based balance-of-plant components in PEWE systems, and results in both performance decay^{32,33} and the chemical degradation of the PEM.^{37,44}

The data provided by neutron radiography experiments hinted at the possibility to introduce a regenerating solution with low pH only in the cathode cell compartment, as most of the cationic impurities are 'pushed' to the cathode CL during PEWE operation. Therefore, performance regeneration of a Fe-contaminated PEWE cell was attempted using a CO₂-pressurized cathodic water loop. The effects of

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Figure 1. Experimental path used in this study. The operando neutron imaging at the SINQ beamline experiment was used to track the position of the Gd^{3+} contaminant in the CCM cross-section during constant current experiments at 1 A cm^{-2} (Gd was selected due to its high neutron attenuation coefficient). A second series of experiments with the Fe^{3+} contaminant were conducted to study the effects of a more common contaminant on the cell overpotentials. Findings on the position of the contaminant from the neutron imaging experiment were used as input to formulate a performance regeneration strategy by utilizing pressurized CO_2 to acidify the cathodic water loop and reprotonate the CCM of the Fe-contaminated PEWE cell.

performance regeneration are quantified through the changes in cell overpotentials.

Experimental

Experiments presented in this work have been organized according to the schematic in Figure 1. Firstly, the neutron imaging experiments were carried out in order to track the Gd^{3+} contaminant in the CCM cross-section during the contamination pro-

cess. The reason for choosing Gd^{3+} is its extremely high neutron cross-section per atom of 50'000 barns (in comparison, a molecule of water, which is already a strong neutron scatterer, has a cross-section of 150 barns).⁴³ Thus, a high contrast can be achieved even with a very small amount of Gd^{3+} present in the PEM. A custom-designed PEWE cell and a mobile, in-house developed electrolyzer test-bench were used for the neutron imaging experiments due to the constraints of the beamline. Another set of experiments with the Fe^{3+} contaminant were conducted outside the beamline to understand the

Figure 2. Schematic of the CO_2 - regeneration process. Flowing the CO_2 through the cathodic gas-water separator at high pressure leads to the formation of carbonic acid in the cathode water recirculation loop. This triggers the ion exchange with the metallic contaminants from the cathode ionomer. Metallic contaminants are scavenged using an ion-exchanger.

effect of a commonly found contaminant on the PEWE overpotentials. Due to the similarities between the electrochemical behavior of Gd- and Fe-contaminated cells, we assumed that the distribution of the contaminant in the CCM cross-section is similar for the two cases at 1 A cm^{-2} , and formulated a CO_2 -assisted regeneration strategy (Figure 2). A stationary, in-house developed test-bench was used to conduct detailed electrochemical characterization and the operando regeneration of the contaminated CCM. The experimental setups, materials and measurement procedures are described in the following paragraphs.

Neutron imaging experiments.—*Neutron imaging setup and data processing.*—Neutron imaging experiments were carried out at the NEUTRA beamline⁴⁵ at the SINQ facility at PSI. The imaging was done in in-plane configuration with a tilted detector setup and anisotropic beam collimation in order to achieve an enhanced spatial resolution⁴⁶ in the direction across the membrane. Pixel size was $6 \mu\text{m}/\text{pixel}$, but due to blurring effects the effective resolution was reduced to circa $30 \mu\text{m}/\text{pixel}$ in the magnified direction. Detailed information on the tilted detector and neutron radiography setup is published elsewhere,⁴⁷ and the neutron imaging PEWE cell is shown in Figure S1 of the Supplementary Material. Exposure time per image was set to 20 s, which proved to be a good compromise between the amount of counts per image and noise in form of saturated (white) pixels coming from various sources (eg. gamma rays). The saturated pixels were treated by applying the outlier removal filter. Since the contamination proved to be a relatively slow process, the images were averaged in groups of 10 after outlier removal filtering in order to reduce the statistical noise, which finally resulted in a temporal resolution of 3.5 minutes. Neutron images were divided pixel-wise by a reference image in order to isolate the useful signal from the attenuation of the cell components. Reference conditions chosen for presented study were wet anode and dry cathode at OCV state. This way it was possible to avoid the influence of membrane swelling due to humidification, which would introduce post-processing artefacts especially in areas close to interface between PTL and CCM. As a result of asymmetric reference conditions the processed images will show relative neutron transmission stemming from either water content change or the accumulation of Gd ions under the effect the electric field.

Materials and cell components.—Electrodiffusion of ionic contaminant in the CCM was observed by introducing a solution of ultrapure water (18.2 MOhm) with dissolved Gd^{3+} ($\text{Gd}_2(\text{SO}_4)_3$, Sigma Aldrich) into the anode feed loop. PEWE cells with a 1 cm^2 active area were assembled with commercial Nafion 117-based CCMs from Greenerity (Ir-based anode and Pt-based cathode) and T10 Ti-sintered PTLs from GKN. CCMs were assembled in the wet state after immersion in ultrapure water for 12 h before the experiments.

Measurement procedures.—PEWE cells were operated with 0.1 mM Gd^{3+} in the anode feed water for 2 h and subsequently for another 2 h with ultrapure water. During the whole experiment, including the run-in period, the current density of the electrochemical cell was set to 1 A cm^{-2} using a Biologic SP-300 potentiostat equipped with a 10 A current booster card and an impedance analyzer. Electrochemical impedance spectroscopy (EIS) was conducted galvanostatically at a DC current density of 1 A cm^{-2} from 10 kHz to 100 mHz with a superimposed 100 mA cm^{-2} AC perturbation current. The temperature of the cell and feed water loop was kept at 50°C using a digital temperature controller. Two feed water tanks were installed, where one contained the dissolved Gd^{3+} in ultrapure water and the other one ultrapure water. Each of the tanks was connected to a tube with the intermediate section leading to the waste tank to allow purging of the line when switching the anode feed water between 0.1 mM Gd^{3+} and ultrapure water to avoid cross-contamination. The anode and cathode pressure was kept at ambient level throughout the experiment.

Fe^{3+} contamination and regeneration setup.—*Materials and cell components.*— $\text{Fe}_2(\text{SO}_4)_3$ salt (Sigma Aldrich) was dissolved in ultra-

pure water to obtain a 0.5 mM Fe^{3+} solution. PEWE cells with a 25 cm^2 active area were assembled with commercial Nafion 117-based CCMs from Greenerity (Ir-based anode and Pt-based cathode) and T10 Ti-sintered PTLs from GKN. CCMs were assembled in the wet state after immersion in ultrapure water for 12 h before the experiments.

Measurement procedures.—An in-house developed test-bench equipped with a Biologic SP-150 potentiostat and a VMP3B-80A booster were used to conduct Fe^{3+} contamination and CO_2 regeneration experiments. Ultrapure water and contaminating solution containing 0.5 mM Fe^{3+} were fed to the anode cell compartment using two feed loops and a peristaltic pump (Ismatec Ecoline Easyload II) at 800 ml min^{-1} . The CCM was conditioned at 40°C for 12 h at 1 A cm^{-2} prior to Fe^{3+} injection. EIS spectra were collected continuously from 10 kHz to 300 mHz at 1 A cm^{-2} with 100 mA cm^{-2} perturbation current during the contamination and regeneration phase. Polarization curves were recorded galvanostatically by cycling the current density stepwise between 2 and 0.04 A cm^{-2} in an upward and downward fashion to capture a hysteresis that might be associated with the electrodiffusion of cationic impurities. All measurements during the contamination sequence were performed at 40°C and atmospheric pressure. After the beginning of life (BoL) polarization curves were recorded, the anode feed was changed from ultrapure water to water with 0.5 mM Fe^{3+} . A detailed overpotential breakdown according to the Tafel model for PEWE was used to quantify the effects of the contaminant on the ohmic (η_{ohm}), kinetic (η_{kin}) and the mass-transport (η_{mtx}) overpotential.^{11,48,49}

CO_2 regeneration procedure.—A stream of CO_2 was injected into the cathode gas-water separator vessel to form carbonic acid (H_2CO_3) and reduce the pH of the water. Cathode pressure was varied between 10 and 21 bar_a to increase the solubility of CO_2 in water. Considering the solubility of CO_2 in water at different pressures and temperatures,^{42,50} the pH of the reprotonating solution is expected to be approximately 3.2 at 21 bar_a and 40°C . Low solubility of CO_2 in water at standard conditions is what makes this method especially attractive. Once the regeneration procedure is complete, simply depressurizing the cathode compartment will bring the pH back to neutral and avoid potential accumulation of residual regenerating acidic medium. A cation exchange resin in proton form was introduced in the cathode recirculation loop to scavenge the Fe-ions and maintain the pH of the water. The anode gas outlet was analyzed for traces of H_2 using an Eaton K1550 gas analyzer to ensure safe PEWE operation. Post-regeneration polarization curves were again recorded at atmospheric pressure.

Results and Discussion

Neutron imaging of electrodiffusing species.—The signal from the anode PTL in Figure 3a shows as bright areas in the radiogram, which indicates an increase in the transmission of neutrons, in particular near the CCM/PTL interface. This is caused by gas (oxygen, with % level crossover hydrogen) that filled a certain fraction of pore volume in the PTL by displacing the water, thereby reducing neutron attenuation. The PTL on the cathode side, however, had been filled with water transported to the cathode by electro-osmotic drag during the experiment, which shows as a decrease of transmission. As for the membrane area, we assume that the CCM has been fully humidified before starting experiment and any change in the signal related to the membrane can be considered an influence of the contaminant.

Thanks to the in-plane configuration and high resolution of the imaging setup it is possible to pinpoint the CCM/PTL interfaces of both cell compartments and observe accumulation of contaminant. After 2.5 h of operation a very distinct line appears at the cathode CL and PTL interface, as a result of Gd-cation accumulation in the cathode CL ionomer (Figure 3a). Similar behavior of cationic species has been observed in post-mortem fuel cell membrane electrode assemblies in a cerium ion migration study.⁵¹ In this study, migration of cationic species in the CCM of an operating PEWE cell is captured

Figure 3. a) Neutron radiograms of an operating PEWE cell during Gd^{3+} contamination. The dark line indicates the accumulation of Gd^{3+} in the cathode catalyst ionomer during operation at 1 A cm^{-2} . b) Polarization curves measured during Gd^{3+} contamination at 60°C and 1 bar_a . c) EIS spectra obtained during the Gd^{3+} contamination measured at 1 A cm^{-2} and 60°C .

for the first time using neutron imaging. The appearance of the Gd signature on the cathode side catalyst layer vicinity is accompanied by an increase of the voltage losses in polarization curves (Figure 3b). In total, the PEWE cell was operated with the anode feed of 0.1 mM Gd^{3+} for 2 h. The full voltage profile during the neutron imaging experiment is given in Figure S2 of the Supplementary Material. The EIS technique was employed to help assign the origin of the overpotential. The high frequency resistance (HFR), which is indicative of ohmic losses, is $\sim 18\%$ ($50 \text{ m}\Omega \text{ cm}^2$) higher after 1 h of PEWE operation on contaminated feed water compared to the beginning of experiment due to Gd^{3+} cations occupying sulfonic acid exchange sites in the ionomer. The HFR does not increase significantly until the end of experiment (Figure 3c). On the other hand, the total cell polarization resistance (low frequency intercept, from the combined effect of the charge transfer and mass transport resistances) increases throughout the contamination experiment.

Neutron imaging experiments provide information about the relative position of the cationic contaminant in the CCM cross-section during the galvanostatic operation of the PEWE cell. Since the radiograms with Gd^{3+} suggest that the ionomer of the cathode CL holds most of the contaminant at high current densities, a regeneration strategy is envisioned to re-protonate the ionomer of the operating PEWE cell by triggering the ion exchange via a low-pH solution introduced only to the cathode cell compartment. The EIS measurements with the contaminated CCM support the findings from neutron imaging, as the HFR was less affected than the polarization resistance during the galvanostatic operation. More detailed electrochemical characterization and evaluation of losses in a contaminated PEWE cell has been conducted using Fe^{3+} contaminant in a setup specifically designed for studying performance losses.

The effects of Fe^{3+} electrodiffusion on voltage losses.—A hysteresis appears in the polarization curve of a contaminated electrolyzer as

a result of the Fe^{3+} migration and diffusion in the CCM (Figure 4a). The EIS spectra measured at 1 A cm^{-2} during the contamination process (Figure 4b) indicate an increase of both HFR and the total cell polarization resistance (including mass transport and kinetic losses), similarly to the spectra collected during the Gd^{3+} neutron imaging experiment. A decrease in minimum current density and thereby cell voltage during the polarization curve measurement (Figure S3) causes an increase of the hysteresis (ΔE_{cell}) at given current density between the forward and backward scan). The changing potential gradient in the ionomer affects the migrative flux of Fe^{3+} towards the cathode catalyst, where it is reduced to Fe^{2+} because $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.77 \text{ V}$. Diffusive flux of Fe from the saturated cathode ionomer at low current density allows the Fe ions to partially back-diffuse into the PEM.⁵² The electrodiffusion-driven changes of the Fe^{3+} distribution in the CCM can trigger different losses and could be responsible for the hysteresis behavior in the polarization curve measurements of the ionically contaminated PEWE. If the contaminant resides mostly in the cathode CL at high cell voltage (as a result of higher current densities), it is expected to result in an increase in kinetic losses of the hydrogen evolution reaction (HER) rather than the losses related to proton conduction in the membrane. At lower cell voltage, the contaminant would partially diffuse into the membrane and shift the distribution of loss terms from kinetic to membrane transport. Therefore, variation of the cell voltage during the polarization curve would in turn cause different distribution of the ionic contaminant in the CCM and lead to a voltage hysteresis. Polarization curve breakdown into voltage loss terms is conducted to investigate the effects of electrodiffusion of Fe-ions and gain better understanding of the hysteresis behavior. A full cell voltage profile during the Fe^{3+} contamination experiments is shown in Figure S4 of the Supplementary Material. Due to the similar effect of Gd on the cell voltage, EIS and polarization curves, it is reasonable to expect that the overpotentials of a Gd-contaminated cell are affected in the same manner as with the Fe-contaminant.

Figure 4. a) Polarization curves of a Fe^{3+} contaminated PEWE cell, compared to the BoL measured at 40°C and 1 bar_a . The down-scan is indicated by solid and the upscan by empty symbols. b) EIS spectra collected at 1 A cm^{-2} during the contamination process with Fe^{3+} .

High-frequency resistance.—A PEWE anode feed with a solution with 0.5 mM Fe^{3+} results in a cell voltage increase of 275 and 485 mV at 1 A cm^{-2} during the polarization curve up- and down-scan, respectively (Figure 4a). The HFR contribution to this difference is approximately 25 mV (Figure 5a). Interestingly, the HFR during the measurement of the polarization curve is lower for the contaminated CCM than for the pristine CCM at BoL between 1.5 and 2 A cm^{-2} (Figure 5a), which could either result from the higher waste heat production with larger overpotential or an effective thinning of the membrane due to CCM creep.³¹ The HFR exhibits a hysteresis as well, between 0.1 and 1.5 A cm^{-2} . Fe^{3+} resides in the cathode CL at high current densities,³³ as observed for Gd^{3+} with neutron imaging. The HFR in this case is less affected, as it mainly stems from the PEM resistance.⁴⁸ Partial diffusion of Fe^{3+} back into the PEM at lower current densities triggers the increase of the HFR during the upward scan of the polarization curve (Figure 5a).

Ionic and total mass transport resistance.—The cell voltage is iR -corrected (Figure 5b) and further analyzed using the Tafel model in order to distinguish between the kinetic and mass transport losses. The mass-transport losses (η_{mtx}) in PEWE consist of contributions from the anode ($\eta_{\text{CLa}}^{\text{H}^+}$) and cathode ($\eta_{\text{CLc}}^{\text{H}^+}$) catalyst layer proton transport resistances,^{53–56} and the contributions from the other cell components (η_{rest}).^{11–13,49}

$$\eta_{\text{mtx}} = \eta_{\text{CLa}}^{\text{H}^+} + \eta_{\text{CLc}}^{\text{H}^+} + \eta_{\text{rest}} = i \cdot (R_{\text{CLa}}^{\text{H}^+} + R_{\text{CLc}}^{\text{H}^+}) + \eta_{\text{rest}} \quad [1]$$

Figure 5. a) iR -free potential and b) HFR for the BoL and the Fe^{3+} contaminated PEWE cell at 40°C and 1 bar_a .

In an uncontaminated electrolyzer cell, the losses associated to ionic transport in the catalyst layers are dominated by the proton transport resistance in the anode catalyst layer ($\eta_{\text{CLa}}^{\text{H}^+}$).^{53,55} The proton transport losses in the cathode catalyst layer ($\eta_{\text{CLc}}^{\text{H}^+}$) is thought to be negligible, due to the low kinetic overpotential of the hydrogen electrode.⁵³ Since the Gd^{3+} experiments have revealed that the ionic contaminant mostly resides in the cathode catalyst layer during constant current operation, the proton transport resistance of the cathode CL ($R_{\text{CLc}}^{\text{H}^+}$) is expected to increase, and thereby the $\eta_{\text{CLc}}^{\text{H}^+}$. The anode CL would be free of contaminant at higher cell potentials, as observed in the neutron radiograms. The contribution of $\eta_{\text{CLa}}^{\text{H}^+}$ at higher current density, and the resulting cell voltage, would not increase in the case of the contaminated sample since the ionic contaminant is mostly occupying the cathode CL. η_{rest} is not expected to change in the presence of the ionic contaminant, since it is not ionic in origin.⁵⁴ Electrodiffusion of Fe^{3+} under the effect of the varying electric field affects the magnitude of $\eta_{\text{CLc}}^{\text{H}^+}$, yielding a large hysteresis of η_{mtx} during the polarization curve measurements (Figure 6).

Proton transport resistances of catalyst layers can be calculated from the electrochemical impedance spectra collected in the H_2/N_2 regime.^{55,56} Using the method from Reference 56, $R_{\text{CLa}}^{\text{H}^+}$ is found to increase up to 137 mOhm cm^2 during contamination, resulting in a 137 mV contribution of the ionic transport to η_{mtx} at 1 A cm^{-2} (see Supplementary Material, Figure S5). The H_2/N_2 measurements most likely do not reveal the full magnitude of ionic mass transport losses in a contaminated cell, since Fe^{3+} is attracted to the counter/reference electrode (cathode) and leaves the anode CL, leaving $R_{\text{CLa}}^{\text{H}^+}$ unaffected.

Figure 6. Mass-transport overpotential for the BoL and the Fe^{3+} contaminated PEWE cell at 40°C and 1 bar_a .

Moreover, the potential of the working electrode (anode) is below the OER onset potential ($<1.4 \text{ V}$) during the H_2/N_2 measurements, and approximately 1.0 V below the potential window at which η_{mtx} dominates in the overpotential breakdown. At such low cell voltage the content of Fe^{3+} in the PEM is higher than at higher potential during the polarization curve measurements.⁵² This is evident when comparing the HFR obtained from the EIS in the H_2/N_2 regime to the HFR during the polarization curve measurements (both at 10 kHz) (Figure S6). The measured ionic contributions to η_{mtx} are most likely related not only to the proton transport in the anode CL, but to the proton transport to the Pt catalyst in the cathode CL as well. Therefore, by probing the ionically contaminated CCM in the H_2/N_2 regime using EIS, one can determine the total apparent proton transport resistance ($R_{\text{CLa}}^{\text{H}^+} + R_{\text{CLc}}^{\text{H}^+}$), albeit at potentials outside the PEWE operating range. The catalyst ionomer occupancy by iron during the PEWE polarization curve is not fully replicated in the H_2/N_2 regime, and only a fraction of its impact on η_{mtx} can be quantified.

Neutron imaging experiments have confirmed that the ionic contaminant resides mostly in the cathode CL during the operation at 1 A cm^{-2} , and the corresponding cell voltage. The changes in η_{mtx} in a contaminated electrolyzer stem from the changes of $R_{\text{CLc}}^{\text{H}^+}$ due to increasing Fe^{2+} content, while $R_{\text{CLa}}^{\text{H}^+}$ can be assumed constant during the experiment while the contaminated electrolyzer is operating and fed with pure ultrapure water. To determine $R_{\text{CLc}}^{\text{H}^+}$, the total η_{mtx} are corrected for the constant terms, $R_{\text{CLa}}^{\text{H}^+}$ and η_{rest} , under the assumption that these losses remain unaffected by $\text{Fe}^{2+/3+}$ in the CCM, at elevated current densities ($>1 \text{ A cm}^{-2}$). The $R_{\text{CLa}}^{\text{H}^+}$ was obtained from the H_2/N_2 measurements before contamination ($20 \pm 2 \text{ m}\Omega \text{ cm}^2$ at 40°C). The total η_{mtx} of the non-contaminated electrolyzer was subsequently corrected for the $R_{\text{CLa}}^{\text{H}^+}$ to obtain η_{rest} , as the $R_{\text{CLc}}^{\text{H}^+}$ is negligible in this case.^{53,55} The analysis of mass transport losses based on the corrections yields a $R_{\text{CLc}}^{\text{H}^+}$ of a contaminated electrolyzer to increase up to $520 \pm 32 \text{ m}\Omega \text{ cm}^2$, which is almost 3 times higher compared to the value obtained from the H_2/N_2 measurements (Figure S5).

Kinetic overpotential.—In a contaminated electrolyzer, metallic cations populate the exchange sites in the cathode CL ionomer and at the PEM/CL interface, leading to the obstruction of proton transport pathways to the catalytic sites. Furthermore, lowered proton activity caused by the presence of Fe-ions is expected to result in a higher HER overpotential. Electrodifusion of Fe-ions during the measurement of the polarization curve means that the Fe^{2+} content in the cathode ionomer varies with current density, which could explain the offset between the η_{kin} measured during the up- and down-scan (Figure 7).

Figure 7. Kinetic overpotential of the BoL, Fe^{3+} contaminated and CO_2 -regenerated PEWE cell at 40°C and 1 bar_a .

The effect of the reduced proton activity on the η_{kin} can be calculated from the fraction of the cathodic CL populated by Fe-ions, and the subsequent change of the pH. The occupancy of the exchange sites by the cations in the membrane as molar fraction ($X_{\text{Fe}^{3+}}$) can be determined using Equations 2 and 3, where κ_{PEM} is the ionic conductivity of the membrane, $\Lambda_{\text{H}^+}^{\text{eff}}$ and $\Lambda_{\text{Fe}^{3+}}^{\text{eff}}$ the effective molar conductivities of the ionic species and $c_{\text{SO}_3^-}$ ⁵⁷ the concentration of the ion-exchange groups in Nafion. Since Fe^{3+} is reduced to Fe^{2+} in the cathode CL, $\Lambda_{\text{Fe}^{3+}}^{\text{eff}}$ will be replaced by $\Lambda_{\text{Fe}^{2+}}^{\text{eff}}$ for the calculation of $X_{\text{Fe}^{2+}}$ in the cathode ionomer (Equations 4 and 5).

$$\kappa_{\text{PEM}} = c_{\text{SO}_3^-} (\Lambda_{\text{H}^+}^{\text{eff}} X_{\text{H}^+} + \Lambda_{\text{Fe}^{3+}}^{\text{eff}} X_{\text{Fe}^{3+}}) \quad [2]$$

$$X_{\text{H}^+} + 3X_{\text{Fe}^{3+}} = 1 \quad [3]$$

$$\kappa_{\text{CLc}} = c_{\text{SO}_3^-} (\Lambda_{\text{H}^+}^{\text{eff}} X_{\text{H}^+} + \Lambda_{\text{Fe}^{2+}}^{\text{eff}} X_{\text{Fe}^{2+}}) \quad [4]$$

$$X_{\text{H}^+} + 2X_{\text{Fe}^{2+}} = 1 \quad [5]$$

The values for the $\Lambda_{\text{H}^+}^{\text{eff}}$, $\Lambda_{\text{Fe}^{2+}}^{\text{eff}}$, $\Lambda_{\text{Fe}^{3+}}^{\text{eff}}$ are calculated by dividing the conductivity of H^+ , Fe^{2+} , Fe^{3+} -exchanged Nafion membrane ($\kappa_{\text{Nafion}}^{\text{H}^+}$, $\kappa_{\text{Nafion}}^{\text{Fe}^{2+}}$, $\kappa_{\text{Nafion}}^{\text{Fe}^{3+}}$) by the concentration of ionic species (c_{H^+} , $c_{\text{Fe}^{2+}}$, $c_{\text{Fe}^{3+}}$). $\kappa_{\text{Nafion}}^{\text{H}^+}$ and $\kappa_{\text{Nafion}}^{\text{Fe}^{3+}}$ values are extracted from the literature, 100.0 ± 0.2 and $5.8 \pm 0.2 \text{ S cm}^{-1}$, respectively.^{57,58} To our knowledge, there is no data for Fe^{2+} -exchanged Nafion in the literature. We therefore approximated $\kappa_{\text{Nafion}}^{\text{Fe}^{2+}}$ with $\kappa_{\text{Nafion}}^{\text{Ca}^{2+}} = 14.0 \pm 1.4 \text{ mS cm}^{-1}$,⁵⁹ due to their similar effect on the limiting molar ionic conductivity in Nafion. $c_{\text{SO}_3^-}$ is divided by 2 and 3 for Fe^{2+} and Fe^{3+} , respectively, to account for the higher valence state of Fe-ions. κ_{PEM} is obtained by dividing the membrane thickness ($d_{\text{PEM}} = 191 \mu\text{m}$, measured before the assembly) by the HFR in Figure 4b (at 1 A cm^{-2}), while κ_{CLc} can be calculated by dividing the $R_{\text{CLc}}^{\text{H}^+}$ by the nominal thickness of the catalyst layer ($10 \mu\text{m}$, from the microscopy work in the Reference 55, in the Supplementary Material).

Using this approximation, the calculated $X_{\text{Fe}^{3+}}$ of the membrane is found to increase up to $12 \pm 1\%$ during the contamination process at 1 A cm^{-2} (Figure 8). $X_{\text{Fe}^{3+}}$, derived from the HFR measurements, appears to reach steady-state values already after 25 min of contamination, and varies by $\sim 2\%$ between the up- and down-scan. $X_{\text{Fe}^{2+}}$, derived from $R_{\text{CLc}}^{\text{H}^+}$ in the cathode CL increases from 6 ± 4 to $44 \pm 1\%$ (Figure 8). The difference between the $X_{\text{Fe}^{2+}}$ values of $22 \pm 1\%$ during the up- and the down-scan reflect a large hysteresis in η_{mtx} .

Figure 8. Left: Molar fraction of the ionomer in the PEM (red) and the cathode catalyst layer (black); Right: Calculated (black) and measured (blue) kinetic overpotential at 1 A cm⁻² of the hydrogen evolution reaction during the polarization curve up- and down-scan, at 40°C and different contamination times with 0.5 mM Fe³⁺.

Swings of the proton activity (a_{H^+}) in the cathode CL due to electrodiffusion of ionic contaminants affect both the thermodynamic and the kinetic overpotential (η_{kin}^{HER}) of the cathode half-reaction. However, the pH gradient will also lead to a potential gradient in the membrane, thereby compensating the change in the thermodynamic overpotential. At higher occupancy by the contaminant, the lowered a_{H^+} will result in increased η_{kin}^{HER} . Kucernak and Zalitis⁶⁰ have estimated that the dependence of the HER/HOR exchange current density (i_0) on a_{H^+} follows the relation:

$$\frac{\partial \log(i_0)}{\partial \log(a_{H^+})} = -\frac{\partial \log(i_0)}{\partial pH} = 0.4 \quad [6]$$

The pH in the cathode CL can be calculated from $X_{Fe^{2+}}$:⁵²

$$pH = -\log(c_{SO_3^{2-}}(1 - 2 \cdot X_{Fe^{2+}})) \quad [7]$$

A relationship of the change in pH and i_0 can be established between 25 and 240 minutes of contamination using Equation 2 and $X_{Fe^{2+}}$ values:

$$\frac{i_{02}}{i_{01}} = 10^{-0.4 \cdot \Delta pH} \quad [8]$$

Assuming charge transfer coefficients are 0.5, the η_{kin}^{HER} can be written as:⁶¹

$$\eta_{kin}^{HER} = b \cdot \sinh^{-1} \left(\frac{i}{2 \cdot i_0} \right) \quad [9]$$

Following Equation A7 (cf. Appendix A), it is possible to derive and solve an expression that relates η_{kin}^{HER} to different states of the cathode CL ionomer occupancy by Fe²⁺. Results from the overpotential analysis and the calculation are shown in Figure 8. The measured

η_{kin}^{HER} is significantly higher than the η_{kin}^{HER} estimated from the ionomer occupancy by Fe²⁺ (Figure 8). Similarly, the hysteresis behavior is not captured in the calculation based on the Fe²⁺ swings during the polarization curve, especially after 130 min of contamination. The deviation between the values indicates a possible cause of cathode kinetic losses unaccounted for by the analysis. Fe underpotential deposition is not encountered at cathodic PEWE potentials.² On the other hand, the cathodic overpotential has been shown to reach up to -500 mV in contaminated cells,³³ which could lead to the partial unavailability of the Pt for the HER.

Performance regeneration with CO₂.—Neutron imaging experiments have revealed that most of the ionic contaminant resides in the cathodic CL during operation at constant current density. Hence, a regenerating, low pH solution can be introduced only in the cathode cell compartment to trigger the ion exchange and re-protonation of the ionomer in the cathode CL of an operating electrolyzer. In this study, instead of directly injecting dilute acid, the cathode water recirculation loop is acidified by introducing CO₂, outlined schematically in Figure 2. The cathode pressure was elevated since the solubility of CO₂ in water is low at standard conditions.⁵⁰ Dissolved CO₂ reacts with water to form H₂CO₃, which deprotonates to form bicarbonate and decreases the pH of water. The cathodic gas/water separator is pressurized with CO₂ to 21 bar_a, and the carbonated water is circulated through the cathode cell compartment to trigger the ion exchange between the Fe²⁺ in the cathode CL and protons from the H₂CO₃. After 36 h of regeneration the potential stabilized (Figure S5) and polarization curves were measured. The EIS collapsed significantly during the regeneration, indicating a beneficial effect of the regeneration on the polarization resistance and the HFR. Since the effect of the Fe-ion

Figure 9. a) Electrochemical impedance spectra collected at 1 A cm^{-2} during the performance regeneration with CO₂ at 21 bar_a cathode pressure and 40°C compared to the spectra at the BoL and after the contamination with Fe³⁺. Polarization curve (b), iR-free cell voltage (c), mass transport overpotential (d) and kinetic overpotential (e) of a PEWE cell regenerated with a CO₂ stream in the cathodic water loop at 21 bar_a and 40°C compared to the respective data at the BoL and after the contamination with Fe³⁺.

electrodiffusion on the voltage losses had previously been determined, cell potential breakdown is conducted again to quantify the extent of the regeneration using the CO₂ approach.

The effect of regeneration on voltage losses.—The cell potential plateaued and stabilized after ~4 h of contamination and the anode feed was flushed again with ultrapure water several times to ensure that there are no residual contaminants in the pipes and cell flow field plates. Operation of the contaminated electrolyzer with fresh anode ultrapure water feed results in the collapse of the EIS spectra and lower polarization resistance (Figure 9a). The HFR and polarization resistance determined from the EIS shows stable behavior after ~16 h of operation. The polarization curves after 36 h of regeneration with CO₂ saturated water exhibit significantly lower hysteresis (Figure 9b). The Fe³⁺ is not present in large enough quantities in the CCM to affect the magnitude of the HFR during electrodiffusion induced by the polarization curve measurements. The HFR is lower after the regeneration compared to the BoL due to the additional creep of the CCM into the PTL voids at 21 bar_a differential pressure, and the resulting lower con-

tact resistance.³¹ The regeneration procedure with the pH-determining process parameters (21 bar_a, 40°C) results in a ~95% regeneration of the voltage efficiency in the current density range of 1 to 2 A cm^{-2} (Figure 9b). If cell performance is corrected for the creep-induced HFR difference between the BoL and regenerated electrolyzer, ~86% of the voltage efficiency is restored in the same current density range. A regeneration attempt at 10 bar_a cathodic pressure (Figure S7) proved less successful in terms of the restoration of voltage efficiency (~70% from 1 to 2 A cm^{-2}). Elevating the cathode pressure further or decreasing the cathode water loop temperature would increase the solubility of CO₂ and result in lower pH. The regenerated PEWE cell is operated for 24 h with the stable cell potential, indicating that no residual contaminant was present in the system after switching over to ultrapure water feed. The hysteresis is almost completely eliminated from the polarization curve and the HFR. The kinetics and mass transport appear to be more sensitive to the presence of Fe-ions during constant current operation, with the hysteresis still present in the η_{mtx} and η_{kin} , albeit to a significantly lower extent (Figures 9c, 9d and 9e). The kinetics appear to be still affected post-regeneration. Fe-ions might still

be present in a sufficient quantity in the CCM to affect the cathode processes.

Conclusions

The presented work is targeted at understanding the effects of electrodiffusion of non-proton cationic species in the catalyst coated membrane (CCM) of an operating PEWE cell. Furthermore, a non-invasive operando method to extract cationic contaminant is demonstrated. We found that the cationic contaminants reside primarily in the cathode CL ionomer during the constant current operation using operando neutron imaging experiments with a Gd^{3+} -contaminated PEWE cell. A detailed voltage loss breakdown with a contaminated CCM revealed that different types of losses arise depending on whether the ionic contaminant populates the ionomer in the membrane or the catalyst layer. The dependence of mass-transport losses on the electrodiffusion of the cationic contaminant in the CCM supports previous claims that these losses originate from the transport limitations in the catalyst layers. To regenerate an operating electrolyzer, the pH of the cathode water was reduced by pressurizing the cathode system compartment with CO_2 . Excess H^+ undergo an ion exchange process with the contaminant and re-protonate the ionomer, mitigating voltage losses. Approximately 95% of the voltage efficiency was restored by applying the CO_2 regeneration technique to a Fe-ion-contaminated PEWE cell at 21 bar_a and 40°C conditions. The CO_2 regeneration method can be employed to improve the reliability and reduce the voltage losses of a contaminated PEWE system. The same configuration may be employed using “renewable” CO_2 , and feeding the mixture of H_2 and CO_2 to a suitable down-stream Power-to-X process.

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Appendix

Equation 9 can be transformed using the inverse sinh rule to yield the relation

$$\sinh^{-1}\left(\frac{i}{2 \cdot i_0}\right) = \ln\left(\frac{i}{2 \cdot i_0} + \sqrt{\frac{i^2}{4 \cdot i_0^2} + 1}\right) = \frac{\eta_{\text{kin}}^{\text{HER}}}{b} \quad [\text{A1}]$$

which can be further simplified to

$$\frac{i}{2 \cdot i_0} + \sqrt{\frac{i^2}{4 \cdot i_0^2} + 1} = \exp\left(\frac{\eta_{\text{kin}}^{\text{HER}}}{b}\right) \quad [\text{A2}]$$

$$\sqrt{\frac{i^2}{4 \cdot i_0^2} + 1} = \exp\left(\frac{\eta_{\text{kin}}^{\text{HER}}}{b}\right) - \frac{i}{2 \cdot i_0} \quad [\text{A3}]$$

$$\exp\left(\frac{2 \cdot \eta_{\text{kin}}^{\text{HER}}}{b}\right) - 2 \cdot \exp\left(\frac{\eta_{\text{kin}}^{\text{HER}}}{b}\right) \cdot \frac{i}{2 \cdot i_0} + \frac{i^2}{4 \cdot i_0^2} = \frac{i^2}{4 \cdot i_0^2} + 1 \quad [\text{A4}]$$

$$\exp\left(\frac{2 \cdot \eta_{\text{kin}}^{\text{HER}}}{b}\right) - \frac{i}{i_0} \cdot \exp\left(\frac{\eta_{\text{kin}}^{\text{HER}}}{b}\right) = 1 \quad [\text{A5}]$$

$$\frac{i}{i_0} = \frac{\exp\left(\frac{2 \cdot \eta_{\text{kin}}^{\text{HER}}}{b}\right) - 1}{\exp\left(\frac{\eta_{\text{kin}}^{\text{HER}}}{b}\right)} \quad [\text{A6}]$$

Equation A6 can be written for different states of Fe^{2+} occupancy of the ionomer (combination with Equation 8), and the respective HER kinetic overpotentials can be brought into the following relation

$$\exp\left(\frac{\eta_{\text{kin},1}^{\text{HER}}}{b_1} - \frac{\eta_{\text{kin},2}^{\text{HER}}}{b_2}\right) \cdot \frac{\exp\left(\frac{2 \cdot \eta_{\text{kin},2}^{\text{HER}}}{b_2}\right) - 1}{\exp\left(\frac{2 \cdot \eta_{\text{kin},1}^{\text{HER}}}{b_1}\right) - 1} = \frac{i_{01}}{i_{02}} = 10^{0.4 \Delta \text{pH}} \quad [\text{A7}]$$

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References

- U. Babic, M. Suermann, F. N. Büchi, L. Gubler, and T. J. Schmidt, *Journal of The Electrochemical Society*, **164**, F387 (2017).
- M. Carmo, D. L. Fritz, J. Mergel, and D. Stolten, *International Journal of Hydrogen Energy*, **38**, 4901 (2013).
- R. Winkler-Goldstein and A. Rastetter, *Green*, **3** (2013).
- F. N. Büchi, M. Hofer, C. Peter, U. D. Cabalzar, J. Bernard, U. Hannesen, T. J. Schmidt, A. Closset, and P. Dietrich, *RSC Advances*, **4**, 56139 (2014).
- B. Bensmann, R. Hanke-Rauschenbach, G. Müller-Syring, M. Henel, and K. Sundmacher, *Applied Energy*, **167**, 107 (2016).
- M. Götz, J. Lefebvre, F. Mörs, A. McDaniel Koch, F. Graf, S. Bajohr, R. Reimert, and T. Kolb, *Renewable Energy*, **85**, 1371 (2016).
- A. Buttler and H. Spliethoff, *Renewable and Sustainable Energy Reviews*, **82**, 2440 (2018).
- T. J. Schildhauer and S. M. A. Biollaz, *CHIMIA International Journal for Chemistry*, **69**, 603 (2015).
- P. Lettenmeier, S. Kolb, F. Burggraf, A. S. Gago, and K. A. Friedrich, *Journal of Power Sources*, **311**, 153 (2016).
- P. Lettenmeier, S. Kolb, N. Sata, A. Fallisch, L. Zielke, S. Thiele, A. S. Gago, and K. A. Friedrich, *Energy & Environmental Science*, **10**, 2521 (2017).
- H. Ito, T. Maeda, A. Nakano, A. Kato, and T. Yoshida, *Electrochimica Acta*, **100**, 242 (2013).
- S. A. Grigoriev, P. Millet, S. A. Volobuev, and V. N. Fateev, *International Journal of Hydrogen Energy*, **34**, 4968 (2009).
- H. Ito, T. Maeda, A. Nakano, C. M. Hwang, M. Ishida, A. Kato, and T. Yoshida, *International Journal of Hydrogen Energy*, **37**, 7418 (2012).
- Z. Kang, G. Yang, J. Mo, S. Yu, D. A. Cullen, S. T. Retterer, T. J. Toops, M. P. Brady, G. Bender, B. S. Pivovar, J. B. Green, and F.-Y. Zhang, *International Journal of Hydrogen Energy*, **43**, 14618 (2018).
- Z. Kang, J. Mo, G. Yang, S. T. Retterer, D. A. Cullen, T. J. Toops, J. B. Green Jr, M. M. Mench, and F.-Y. Zhang, *Energy Environ. Sci.*, **10**, 166 (2017).
- J. Mo, R. R. Dehoff, W. H. Peter, T. J. Toops, J. B. Green, and F.-Y. Zhang, *International Journal of Hydrogen Energy*, **41**, 3128 (2016).
- E. Oaktan, D. Lebedev, A. Fedorov, F. Krumeich, J. Tillier, O. Sereda, T. J. Schmidt, and C. Coperet, *New Journal of Chemistry*, **40**, 1834 (2016).
- E. Oaktan, D. Lebedev, M. Povia, D. F. Abbott, E. Fabbri, A. Fedorov, M. Nachttegaal, C. Coperet, and T. J. Schmidt, *ACS Catalysis*, **7**, 2346 (2017).
- D. Lebedev, M. Povia, K. Waltar, P. M. Abdala, I. E. Castelli, E. Fabbri, M. V. Blanco, A. Fedorov, C. Coperet, N. Marzari, and T. J. Schmidt, *Chemistry of Materials*, **29**, 5182 (2017).
- K. A. Lewinski, D. F. v. d. Vliet, and S. M. Luopa, *ECS Transactions*, **69**, 893 (2015).
- L. C. Seitz, C. F. Dickens, K. Nishio, Y. Hikita, J. Montoya, A. Doyle, C. Kirk, A. Vojvodic, H. Y. Hwang, J. K. Nørskov, and T. F. Jaramillo, *Science*, **353**, 1011 (2016).
- D. F. Abbott, D. Lebedev, K. Waltar, M. Povia, M. Nachttegaal, E. Fabbri, C. Coperet, and T. J. Schmidt, *Chemistry of Materials*, **28**, 6591 (2016).
- H.-S. Oh, H. N. Nong, T. Reier, M. Gliech, and P. Strasser, *Chem. Sci.*, **6**, 3321 (2015).
- K. E. Ayers, J. N. Renner, N. Danilovic, J. X. Wang, Y. Zhang, R. Maric, and H. Yu, *Catalysis Today*, **262**, 121 (2016).
- A. Albert, A. O. Barnett, M. S. Thomassen, T. J. Schmidt, and L. Gubler, *ACS Appl Mater Interfaces*, **7**, 22203 (2015).
- A. Skulimowska, M. Dupont, M. Zaton, S. Sunde, L. Merlo, D. J. Jones, and J. Rozière, *International Journal of Hydrogen Energy*, **39**, 6307 (2014).
- C. K. Mittelsteadt and J. A. Staser, in *Polymer Science: A Comprehensive Reference*, **10**, 849, Elsevier (2012).
- DOE Technical Targets for Hydrogen Production from Electrolysis, in *Fuel Cell Technologies Office*, U.S. Department of Energy (DOE), Office of Energy Efficiency & Renewable Energy (2015). <https://energy.gov/eere/fuelcells/doe-technical-targets-hydrogen-production-electrolysis> [accessed on 21.01.2019].
- L. Bertuccioli, A. Chan, D. Hart, F. Lehner, B. Madden, and E. Standen, Development of Water Electrolysis in the European Union, (2014). <https://www.fch.europa.eu/node/783> [accessed on February 16-17].
- E. Anderson, *2nd International Workshop on Durability and Degradation Issues in PEM Electrolysis Cells and its Components*, Freiburg, Germany (2016).
- C. Rakousky, U. Reimer, K. Wippermann, M. Carmo, W. Lueke, and D. Stolten, *Journal of Power Sources*, **326**, 120 (2016).
- S. Sun, Z. Shao, H. Yu, G. Li, and B. Yi, *Journal of Power Sources*, **267**, 515 (2014).
- X. Wang, L. Zhang, G. Li, G. Zhang, Z.-G. Shao, and B. Yi, *Electrochimica Acta*, **158**, 253 (2015).
- Q. Feng, X. Z. Yuan, G. Liu, B. Wei, Z. Zhang, H. Li, and H. Wang, *Journal of Power Sources*, **366**, 33 (2017).
- J. Mo, S. M. Steen, F.-Y. Zhang, T. J. Toops, M. P. Brady, and J. B. Green, *International Journal of Hydrogen Energy*, **40**, 12506 (2015).

36. L. Zhang, X. Jie, Z.-G. Shao, X. Wang, and B. Yi, *Journal of Power Sources*, **241**, 341 (2013).
37. H. Liu, F. D. Coms, J. Zhang, H. A. Gasteiger, and A. B. LaConti, in *Polymer Electrolyte Fuel Cell Durability*, F. N. Büchi, M. Inaba, and T. J. Schmidt, Editors, p. 71, Springer-Verlag New York, New York, USA (2009).
38. P. Lettenmeier, R. Wang, R. Abouatallah, B. Saruhan, O. Freitag, P. Gazdzicki, T. Morawietz, R. Hiesgen, A. S. Gago, and K. A. Friedrich, **7**, 44035 (2017).
39. C. Liu, M. Carmo, G. Bender, A. Everwand, T. Lickert, J. L. Young, T. Smolinka, D. Stolten, and W. Lehnert, *Electrochemistry Communications*, **97**, 96 (2018).
40. N. Yoshiyuki, S. Misato, T. Takashi, and T. Mitsuo, *Electrolytic ozonized water producing unit and its regenerating method*, JPH10130876A Kobe Steel Ltd, Japan (1996).
41. H. Yu, S. Sun, Z. Shao, and S. Wei, In-situ regeneration method of solid polymer electrolyte water electrolyzer, CN105603453A, China (2014).
42. C. Peng, J. P. Crawshaw, G. C. Maitland, J. P. Martin Trusler, and D. Vega-Maza, *The Journal of Supercritical Fluids*, **82**, 129 (2013).
43. V. F. Sears, *Neutron News*, **3**, 26 (1992).
44. A. B. LaConti, H. Liu, C. Mittelsteadt, and R. C. McDonald, *ECS Transactions*, **1**, 199 (2006).
45. P. Vontobel and L. Wiezel, *Nondestructive Testing and Evaluation*, **16**, 191 (2001).
46. P. Boillat, D. Kramer, B. C. Seyfang, G. Frei, E. Lehmann, G. G. Scherer, A. Wokaun, Y. Ichikawa, Y. Tasaki, and K. Shinohara, *Electrochemistry Communications*, **10**, 546 (2008).
47. P. Boillat, Advanced characterization of polymer electrolyte fuel cells using high resolution neutron imaging. *Diss. ETH No. 18397* 2009.
48. M. Suermann, T. J. Schmidt, and F. N. Büchi, *Electrochimica Acta*, **211**, 989 (2016).
49. M. Suermann, K. Takanohashi, A. Lamibrac, T. J. Schmidt, and F. N. Büchi, *Journal of The Electrochemical Society*, **164**, F973 (2017).
50. L. W. Diamond and N. N. Akinfiev, *Fluid Phase Equilibria*, **208**, 265 (2003).
51. A. M. Baker, R. Mukundan, D. Spornjak, E. J. Judge, S. G. Advani, A. K. Prasad, and R. L. Borup, *Journal of The Electrochemical Society*, **163**, F1023 (2016).
52. T. A. Greszler, T. E. Moylan, and H. A. Gasteiger, in *Handbook of Fuel Cells*, W. Vielstich, A. Lamm, H. A. Gasteiger, and Y. H. Yokokawa, Editors, chapter 49. John Wiley & Sons, Ltd, (2010).
53. M. Bernt and H. A. Gasteiger, *Journal of The Electrochemical Society*, **163**, F3179 (2016).
54. M. Bernt, A. Siebel, and H. Gasteiger, *Journal of the Electrochemical Society*, **165**, F305 (2018).
55. U. Babic, T. J. Schmidt, and L. Gubler, *Journal of The Electrochemical Society*, **165**, J3016 (2018).
56. U. Babic, E. Nilsson, A. Pătru, T. J. Schmidt, and L. Gubler, *Journal of The Electrochemical Society*, **166**, F214 (2019).
57. S. Slade, S. A. Campbell, T. R. Ralph, and F. C. Walsh, *Journal of The Electrochemical Society*, **149**, A1556 (2002).
58. K. Hongsirakarn, J. G. Goodwin, S. Greenway, and S. Creager, *Journal of Power Sources*, **195**, 7213 (2010).
59. L. Coury, *Curr. Sep.*, 1999, **18**, 3, 92
60. A. R. Kucernak and C. Zalitis, *The Journal of Physical Chemistry C*, **120**, 10721 (2016).
61. V. Janardhanan and O. Deutschmann, *Zeitschrift für Physikalische Chemie*, **221**, 4, 443 (2007).