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Operating an ozone-evolving PEM electrolyser in tap water: A case study of water and ion transport

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ABSTRACT

While PEM water electrolysis could be a favourable technique for *in situ* sanitization with ozone, its application is mainly limited to the use of ultrapure water to achieve a sufficient long-time stability. As additional charge carriers influence the occurring transport phenomena, we investigated the impact of different feed water qualities on the performance of a PEM tap water electrolyser for ozone evolution. The permeation of water and the four most abundant cations (Na⁺, K⁺, Ca²⁺, Mg²⁺) is characterised during stand-by and powered operation at different charge densities to quantify underlying transport mechanisms. Water transport is shown to linearly increase with the applied current (95 \pm 2 mmol A⁻¹ h⁻¹) and occurs decoupled from ion permeation. A limitation of ion permeation is given by the transfer of ions in water to the anode/PEM interface. The unstabilized operation of a PEM electrolyser in tap water leads to a pH gradient which promotes the formation of magnesium and calcium carbonates and hydroxides on the cathode surface. The introduction of a novel auxiliary cathode in the anolytic compartment has shown to suppress ion permeation by close to 20%.

1. Introduction

Proton exchange membranes (PEM) present versatile constituents that enable efficient electrolyser and fuel cell systems [1–4]. Their sizes and applications range from miniaturized products for domestic use [5,6] to industrial scale applications for chemical energy storage [7–9]. Within the electrochemical cell design, a solid polymer electrolyte features the option to spatially separate both half-cells [10,11], permitting to deal safely even with consumed or evolving gaseous reactants.

Modified electrodes can be used in PEM water electrolysers to enable anodic ozone evolution and *in situ* treatment of an anodic water feed [12–15] or in wastewater treatment [16,17]. These electrochemical cells contain a PEM as a solid polymer electrolyte onto which oppositely charged electrodes are firmly pressed, forming a membrane-electrode assembly (MEA) [12,18–21]. Water is supplied to both reaction compartments and electrolytically decomposed at the surfaces of the electrodes [18,22]. Anodically, water molecules are oxidized to both oxygen and ozone gas (eq. (1) and (2)) which can immediately dissolve in the surrounding electrolyte. The remaining protons are subsequently transported through the PEM, discharged, and recombine at the cathode surface to form hydrogen gas (eq. (3)). As the anodic formation of O_2 during PEM water electrolysis is thermo-dynamically preferential, significant amounts of O_3 can only be generated when a specific catalytically active anode surface with a high overpotential for O_2 evolution is chosen (e.g. β -PbO₂) [23].

Anode:

 $2 H_2 O \rightarrow O_2 + 4 H^+ + 4 e^- (E^0 = +1.23 V vs. NHE)$ (1)

 $3 H_2 O \rightarrow O_3 + 6 H^+ + 6 e^- (E^0 = +1.51 V \text{ vs. NHE})$ (2)

Cathode:

$$2 H^+ + 2 e^- \rightarrow H_2(E^0 = \pm 0.00 V vs. NHE)$$
 (3)

Within the cell the current is transported by ionic conduction in the solid polymer electrolyte, which most often consists of a NafionTM membrane [24,25]. Following the cluster-network model, initially proposed by Hsu and Gierke, the NafionTM bulk material consists of a

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hydrophobic PFSA backbone and functional sulfonate groups, which self-organize to form hydrophilic spheres (inverted micelles) of about 4 nm in diameter, connected by cylindrical channels of about 1 nm in diameter [26,27]. All mass transport through the PEM occurs within these ion channels [28,29]. As a result of the large number of sulfonate side-groups in its chemical structure, NafionTM shows a selective permeability to cationic species, while anions are not actively transported due to Donnan exclusion [24,30] and thus acts as an ion-selective barrier.

Previously, the transport of water, gases and ions in PEM cells has been characterised during the operation of fuel cells [31–33], redox flow batteries [34–36] and chlor-alkali electrolysis [37]. However, in recent literature, these phenomena are mostly investigated by means of simulational studies only. All mass transport processes occurring in PFSA membranes strongly depend on local and global membrane properties, as e.g. the polymer structure or hydration state of the membrane [38]. As described by the Nernst-Planck model [39,40], the overall ion transport is mainly comprised of two superimposed mechanisms, schematically depicted in Fig. 1: Diffusion (Fig. 1(a)) through the membrane *via* ion exchange (for H⁺ also referred to as "proton hopping" or Grotthuss mechanism) and additional ion migration (Fig. 1(b)) induced by the electric field gradient across the membrane [28,41]. In operation, both these driving forces act upon all permeating ions.

As tap water contains additional charge carriers, such as mono- and bivalent cations (Na⁺, K⁺, Ca²⁺, Mg²⁺), they may equally be transported through the membrane due to their physicochemical properties and the electric field applied during electrolysis [32,33,42]. However, strong interactions between these cations and the sulfonate groups in the membrane may prevent a regular vehicular transport if the membrane exhibits a low local water content. This state then leads to a different "hopping" mechanism being more related to site-to-site hopping processes as observed in solids [43]. Nevertheless, as the membrane is continuously exposed to water on both sides, an insufficient hydration state can be considered unlikely when dealing with a PEM water electrolyser.

Despite dragging water electro-osmotically across the membrane into the catholytic compartment [24,30,44], this permeation behaviour leads to an accumulation of ions in the catholyte and ultimately results in the formation of precipitates, impairing the performance of both membrane and electrodes. As the long-term stability of the PEM electrolyser depends on the elemental composition of the supplying water, the application of this technology has been limited to the *in situ* ozonation of ultrapure water distribution systems only.

Therefore, this study covers the permeation behaviour of both water and the four most abundant cations in tap water within an ozoneevolving PEM electrolyser under different operation conditions to account for different water feed qualities and demands for disinfection. Special emphasis is put on the unique characteristics during the batchlike operation in stagnant water supplies and its relations to pH environment, precipitation formation and constructional mitigation of ion permeation. As a result, preferential operational modes to enhance the long-term stability of such a sanitization device are identified and amended by physicochemical parameters which can be directly used for scaled-up applications.

2. Materials and methods

To investigate both ion and water permeation during the operation of a PEM tap water electrolyser, the setup depicted in Fig. 2 was used for all experiments. Within a PVC housing a hexagonally arranged structured membrane-electrode assembly (SMEA) is mounted, consisting of up to seven pairs of PbO₂-coated porous titanium anodes $(A_{geo} = 0.2 \text{ cm}^2)$ per electrode) and porous titanium cathodes (all Innovatec Gerätetechnik GmbH, Rheinbach, Germany). Individual water supplies for each half-cell allow for an independent study of both the cathodic and anodic water cycle, seperated by a Nafion[™] 117 membrane (DuPont, Wilmington, Delaware, USA) as PEM material (total membrane area exposed to solution: $A_{geo} = 33.2 \text{ cm}^2$). For experiments with technical suppression of permeation an additional titanium auxiliary cathode was placed inside the analytic compartment and electrically connected to the other cathodes placed in the catholytic compartment. Due to a PTFE spacer only the SMEA array of electrodes is in direct contact with the PEM.

The compositions for synthetic tap water samples for anolytic circulation are demonstrated in Table 1 and account for different levels of water hardness. All solutions were prepared in accordance with the German Detergents and Cleaning Products Act (German designation WRMG [45]) using p.a. grade NaCl, MgCl₂ · 6 H₂O (both Carl Roth, Karlsruhe, Germany), KCl, CaCl₂ · 2 H₂O (both Merck, Darmstadt, Germany) and 18.2 MΩ ultrapure water using ELGA Purelab Flex (VWS, High Wycombe, UK).

To avoid precipitation within the catholytic water cycle, a 100 mmol L^{-1} HAc / NH₄Ac buffer system (pH = 4.7) (Carl Roth, Karlsruhe, Germany) was used. Before every experiment, the PEM was regenerated without electrodes and converted to its $\rm H^+$ form by boiling it in 1 mol L^{-1} H₂SO₄ (Carl Roth, Karlsruhe, Germany) for 1 h and equilibrated in deionized water.

Standard operation parameters of the electrolysis cell were set to a current density of 1.00 A cm^{-2} , referring to a geometric anode surface of 1.4 cm², medium water as the anolyte and 8 h of operation. For the



Fig. 1. (a) Diffusive ion transport *via* dynamic ion exchange driven by a concentration gradient. With no current applied, diffusing ions (X^{n+}) have to be compensated by back-diffusion of buffer ions (B^+) to maintain electroneutrality. After reaching ion exchange equilibrium, all SO₃ groups are associated with X^{n+} ions. Further permeating ions experience a dynamic exchange and pass the membrane through ion channels. **(b)** Migration through the membrane by vehicular transport. In the electric field, hydrated ions cross the PEM towards the anode. Own drawing, adapted from [27].



Fig. 2. Scheme of the experimental setup (left) and arrangement of the SMEA (right). Synthetic tap water from the reservoir is pumped through the anodic half-cell of the PEM electrolyser, with ions permeating into the buffered cathodic water cycle. For selected operation modes, the electrolyser can be equipped with an auxiliary cathode in the analytical compartment.

Table 1

Composition of synthetic tap water samples with varying cation concentrations used for permeation experiments, given as mass concentrations β_{ion} and equivalent concentrations $c_{ion,\ eq}$ (expressed in milliequivalents (mEq) per litre) as well as molar equivalent fractions $x_{ion,\ eq}$.

Water hardness level	soft		medium		hard		
	$\begin{array}{c} \beta_{ion} / \\ mg \\ L^{-1} \end{array}$	c _{ion, eq} ∕ mEq L ^{−1}	$\frac{\beta_{ion}}{mg} / \\ L^{-1}$	c _{ion, eq} ∕ mEq L ^{−1}	$\frac{\beta_{ion}}{mg} / \\ L^{-1}$	c _{ion, eq} ∕ mEq L ^{−1}	x _{ion, eq} / Eq- %
Na ⁺	20.0	0.87	40.0	1.74	80.0	3.48	24.2
K ⁺	2.5	0.06	5.0	0.13	10.0	0.26	1.8
Mg ²⁺	8.0	0.66	16.0	1.32	32.0	2.63	18.3
Ca ²⁺	40.0	2.00	80.0	3.99	160.0	7.98	55.6
Σ	70.5	3.59	141.0	7.18	282.0	14.35	100.0

aforementioned water hardness levels, permeation during electrolysis was observed for current densities applied from 0.25 to 1.25 A cm⁻² (denoted "powered operation"). In order to simulate a typical stand-by operation in a low-power mode, an additional level of 0.01 A cm⁻² (for anodic protection of the catalytically active PbO₂ layer) was evaluated.

After defined time intervals, 5 mL of the catholyte were sampled for subsequent quantification of permeated ions, which was carried out using an ARCOS ICP-OES system (Spectro, Kleve, Germany) in radial configuration, equipped with a standard Scott spray chamber, a cross-flow nebulizer and certified elemental standards (Carl Roth, Karlsruhe, Germany). Operation conditions for ICP-OES measurements are listed in Table 2.

Water permeation was quantified gravimetrically using a Ranger 3000 balance (Ohaus, Parsippany, New Jersey, USA) with a data acquisition rate of 6 Hz.

During pH experiments both the anolytic and catholytic compartments were continuously purged with Argon 4.8 gas (Westfalen AG, Münster, Germany) at 30 mL min⁻¹ to minimize atmospheric influences within the open setup.

Non-buffered long-term experiments related to the investigation of scale formation were carried out applying a current density of 1.00 A

Table 2

Operation conditions for ICP-OES measurements in radial configuration.

Parameter	
Incident power / W	1,400
Cooling gas flow rate / $L min^{-1}$	13.0
Auxiliary gas flow rate / L min $^{-1}$	1.5
Nebulizer gas flow rate / $L min^{-1}$	0.70
Rinse time / s	60
Integration time / s	12
Number of replicates	4

 $\rm cm^{-2}$ and using hard model water prepared as stated above. Experiments were conducted for 500 operating hours before disassembly and subsequent analysis.

X-ray diffraction (XRD) analysis and characterisation of scale particles were carried out on a D2 PHASER diffractometer and using TOPAS 5.0 software (both Bruker, Billerica, Massachusetts, USA). Analyses were performed at U = 30 kV and I = 10 mA within a 20 range from 5° to 65° using a Cu-K_{α} radiation source ($\lambda = 1.54$ Å).

For identification of the cathodic surface composition, an X-Supreme 8000 (Oxford Instruments, Abingdon, United Kingdom) X-ray fluorescence (XRF) spectrometer was used at U = 15 kV, I = 10 μA and 180 s integration time.

The spatial distribution of characteristic elements on the cathode surfaces was determined using a JEOL 7200F field-emission scanning electron microscope (SEM) at U = 10 kV. Corresponding elemental mapping analyses were obtained using a Bruker XFlash& 6|60 EDX detector.

3. Results and discussion

3.1. Water transport within a PEM electrolyser

During the operation of a PEM electrolyser in water, positive charge carriers are transported from the anolytic to the catholytic compartment through the PEM. As cations in aqueous solution are present in hydrated form, the ion transport is accompanied by an electro-osmotic flow of water, i.e. an increase of the water volume within the catholytic compartment. Fig. 3(a) shows that the amount of permeated water n_{H_2O} increases linearly ($R^2 > 0.99$ for J > 0.25 A cm⁻², $R^2 = 0.95$ for J = 0.25 A cm⁻²) with the operating time of the electrolyser. While no significant water permeation was measured in stand-by operation, a raise in current density is directly accompanied by increased levels of permeating water. This observation strongly suggests that substantial water transport is occurring predominantly due to ion migration and electro-osmosis between the electrodes. With a higher current density, more charge carriers are produced and transported per unit time, thus leading to an expedited increase in catholytic water volume.

By linear regression of n_{H_2O} in Fig. 3(a) water permeation rates \dot{n}_{H_2O} can be obtained to quantify the occuring electro-osmotic drag. The data given in Table 3 yield an excellent fit to a linear function to describe the observed correlation. Thereof, the change in water permeation rate was determined to $95 \pm 2 \text{ mmol A}^{-1}h^{-1}$ and indicates that the amount of permeating water does not depend on the size of the contacted electrode surface area but is merely proportional to the experimental time and current flow within the PEM electrolyser. However, smaller variations in water transport may also result from the state of the NafionTM membrane, as the electro-osmotic drag (EOD) coefficient is influenced by local hydration state, even under fully hydrated conditions at comparable temperatures [46].



Fig. 3. (a) Cumulated amount of permeated water n_{H_2O} during representative experiments for different current density levels. A linear increase in water permeation can be observed with progressing experimental time and elevating current density. Measured data points form a step profile due to limitations by the balance resolution of 0.5 g (corresponding to 28 mmol H₂O). **(b)** Water permeation rates \dot{n}_{H_2O} for experiments with varying relative ion composition but equal cationic strength. **(c)** Permeation rates for different Mg²⁺ and Ca²⁺ containing mixtures as well as different water hardness levels representing varying equivalent concentrations. No significant deviation from an average value of 96 ± 5 mmol cm⁻²h⁻¹ is observed for anolytic feed waters with individual ion species, mixtures of different elements or even differing water hardness levels.

Table 3	
Water permeation rates \dot{n}_{H_2O} and total ion permeation rates $\sum \dot{n}_{ion, eq}$	for all current densities under investigation.

J /A cm ⁻²		0.01	0.25	0.50	0.75	1.00	1.25	R^2
\dot{n}_{H_2O} /mmol cm ⁻² h ⁻¹		$0.0\ \pm\ 2.5$	$14.0~\pm~2.5$	$37.1~\pm~3.1$	$61.4~\pm~2.5$	$87.6~\pm~7.9$	$107.2~\pm~7.8$	0.9948
$\sum \dot{n}_{ion, eq} / \mu Eq \ cm^{-2} \ h^{-1}$	soft	$4.0\ \pm\ 0.1$	$7.6~\pm~0.2$	$8.0\ \pm\ 0.4$	$8.0\ \pm\ 0.3$	$10.0~\pm~0.3$	$10.4~\pm~0.3$	0.8471
	medium	$7.0~\pm~0.1$	$11.0~\pm~0.2$	$14.3~\pm~0.3$	$16.5~\pm~0.2$	$16.4~\pm~0.3$	$20.9~\pm~0.3$	0.9408
	hard	$13.2~\pm~0.2$	$24.5~\pm~0.5$	$27.1~\pm~0.3$	$31.4~\pm~0.9$	$40.1~\pm~1.2$	$43.5~\pm~1.1$	0.9644

As the electrical charge can only be transported across the membrane by cationic species, the occurring mass transport behaviour must be ascertained for different cation compositions in order to reliably establish this technique for tap water disinfection in regions with diverging levels of water hardness. Fig. 3(b) allows for a comparison of \dot{n}_{H_2O} for anolyte feeds of varying composition and indicates that no significant differences in water permeation are observed with all three water hardness levels under investigation. Consequently, \dot{n}_{H_2O} can be considered as a function independent of the total anolytic cation concentration.

Furthermore, Fig. 3(b) and (c) depict water permeation rates \dot{n}_{H_2O} which were determined for model waters of varying relative ion composition but with equal normality (equivalent concentrations), i.e. all solutions contained the same cationic strength of 7.18 mEq L⁻⁻ corresponding to medium tap water used in this study. This enables to identify whether certain elements contribute in particular to the water transport during the PEM operation as equal amounts of equivalents can be transported by permeating tap water cations (other than H⁺) present in the analytic solutions. For a fixed current density level of 1.00 A cm^{-2} maintained in all experiments, no significant influence was observed when altering the anolytic composition to individual monovalent or bivalent ion species or systematic mixtures thereof. In contrast, previous studies have found considerable differences in the amount of water transported with each permeating charge carrier when the PFSA membrane had been pre-exchanged with different alkali cations before use [47,48]. As a tap water electrolyser makes use of an H⁺ form Nafion[™] membrane in dilute ion solutions, only a partial exchange with tap water cations will take place. Hence, the influence of the state of the membrane is minimized and therefore of minor relevance for the application. Thus, the relative composition of the analytic feed water appears to be of no significance for the water permeation and can be expected to hold

also true for further ions beyond the scope of this study. Hence, the water permeation rates \dot{n}_{H_2O} for all experiments with standard operation at J = 1.00 A cm⁻² were averaged and yielded a mean value of 96 ± 5 mmol cm⁻² h⁻¹, which is in perfect accordance with the findings obtained from Fig. 3(a).

The observed water flux can further be expressed as a net EOD coefficient for each transported charge carrier during cell operation. The obtained mean value of 2.55 ± 0.05 molecules H₂O per charge carrier is in accordance with literature data for various fuel cell and water electrolysis applications which typically range from 2.5 to 2.9 when using fully hydrated NafionTM 117 membranes [46,49,50]. The common interpretation of an EOD > 1 suggests that the transport of water and ions occurs *via* a vehicular mechanism, meaning that fast-moving ions drag their hydration sphere into the catholyte. As has been previously reported, proton hopping or related structural diffusion phenomena do not allow for a net transport of water [51]. Following these implications, it is suggested that diffusive processes do not contribute to water transport under electrolysis conditions. Nonetheless, the correlation of the EOD coefficient with distinct transport phenomena is dealt with controversially in the literature [38,52,53].

3.2. Ion diffusion and migration during powered and stand-by operation

For the investigation into the permeation behaviour of the cationic species, ICP OES measurements were conducted to determine shifting ion concentrations within the catholyte. In order to assess the reliability of the so-obtained data in a first step, all selected methods were examined with respect to the analytical performance of the conducted calibrations. Therefore, limits of detection (LOD) and quantification (LOQ), linearity, precision and accuracy were evaluated for all elements of interest (see supplementary table A.1 in the appendix).

For most of the observed elements, calibrations yield LOD values below 40 μ g L⁻¹, with a minimal value of 11.9 μ g L⁻¹ for Ca. Given that all relevant components can be quantified to trace levels of less than 0.25 mg L⁻¹, confident monitoring of ion migration and diffusion during PEM electrolyser operation is possible. The obtained values for LOD and LOQ are in the same order of magnitude as reported in previous works [54,55], confirming that the chosen methodology is not limiting the analyses of the datasets.

Apart from that, all calibrations were fitted to linear functions with coefficients of determination $R^2 \geq 0.9996$ and precision coefficients of less than 4%. With this method, artificial samples differing in analyte concentrations of merely 0.1 mg L^{-1} can be significantly distinguished.

In a first approach, the obtained ICP OES data enables quantifying the cationic permeation behaviour during standard electrolysis operation in medium tap water, which is depicted in Fig. 4(a). Herein, the molar concentrations of all four observed cations are depicted and illustrate a strictly monotonous increase with experimental time. Notably, the transport behaviour is sufficiently linear for all analytes ($R^2 > 0.995$) within the observed timeframe. As a consequence of the original composition of the anolytic model water, the obtained regression functions for different cationic species deviate significantly in their slope values. Exemplarily, the full dataset for medium water hardness and a current density of 1.00 A cm⁻² is depicted in Fig. A.1 the appendix.

In order to identify trends in transport selectivity through the PEM in Fig. 4(b), the calculated ion permeation rates were normalized by the original molar fractions within the anolyte. The so-obtained values correspond to expected total ion permeation rates if all cations were of one distinct species. It can be seen that transport rates increase significantly for elevated ion concentrations, i.e. increased levels of water hardness. For an ideal limiting current regime, transport is inselective as all ions reaching the anode/PEM interface immediately permeate through the membrane. In the present study, the observations for medium and soft water show that ion selectivities of Na⁺, Mg²⁺, Ca²⁺ are in a comparable order of magnitude whereas K⁺ shows an increased permeability. Even further, for a hard model water, a 15.8% increased permeability of K⁺ could be determined while the permeability of Na⁺ decreased by 11.6%. To further assess whether these trends in relative

ion transport are consistent throughout all water hardness levels, ion permeation rates have also been normalized by their initial equivalent concentrations $c_{ion, eq}$ in the anolyte (see Table 1) and averaged for all investigated water hardness levels. Comparing these permeation values to the respective ion mobility in aqueous media (Fig. 4(c), reference values derived from [56]), a considerable congruence can be noted, when ion concentrations are sufficiently high to unveil significant deviations. This may be a direct consequence of concentration polarization, which causes a local depletion of tap water abundant ions at the PEM/anode interface. When ions from the bulk anolyte diffuse towards the interface, they are discriminated by their respective ion mobility in water.

In consequence, the ion transport selectivity appears to be caused by both the ion mobility in water and the composition of the anolytic feed. Thus, the transfer of ions in water to the anode/PEM interface limits the ion permeation under the given operation conditions in tap water.

To approximate the correlation of water and ion permeation *via* diffusion and migration respectively, the occurring mass transport behaviour was measured at different current density levels, with the corresponding permeation rates given in Table 3.

Both water and ion permeation increase when a higher current density is applied. However, when characterizing the relationship by a linear function, it becomes obvious that for water transport a satisfying correlation can be drawn ($R^2 = 0.9948$) while this is only partially given for ion permeation. With increasing water hardness, R^2 improves from 0.85 to 0.96, referring to an increasingly linear relationship between ion permeation and current density. While water permeation only occurs during powered operation ($J \ge 0.25 \text{ A cm}^{-2}$), i.e. when ion transport is also subject to migration, a significant ion transport can be also observed during stand-by operation ($J = 0.01 \text{ A cm}^{-2}$). In this operational mode, a possible water transport by diffusion across the entire PEM surface could not be observed within the experimental limitations and must therefore be smaller than 105 μ mol H₂O h⁻¹ cm⁻². Hence, water transport appears to be predominantly mediated by migration and not by structural diffusion, in contrast to the joint mechanism model for ion permeation.

In stand-by operation, ions from the analytic compartment infiltrate the PEM mainly by slow diffusive processes and occasionally get exchanged at the SO_3^- groups within the membrane, gradually



Fig. 4. (a) Observed amounts of mono- and bivalent ions, transported from anolytic tap water to the catholytic loop of the PEM electrolyser setup. During electrolysis, a linear transport of all ions can be observed. Corrections for permeation-induced dilution and sampling have been applied. (b) Ion transport rates normalized by their molar fractions $x_{ion, eq}$ (see Table 1) under standard conditions. With increasing water hardness, more tap water cations are transported per time unit. While for medium and soft water hardness transport appears quasi-inselective, a more obvious discrimination can be observed for hard tap water, where K⁺ is preferably transported by approx. 15% over the average transportation rates (dashed lines). (c) Ion transport rates normalized by their initial concentration in the anolyte under standard conditions. For all water hardness levels, the ionic permeation trends (left axis) can be related to their respective ion mobility in water (values derived from [56], right axis).

converting it from its initially charged H^+ - form to its X^{n+} -form. Once the ion exchange capacity of the membrane is exhausted [57,58], further ions get transported to the catholyte by diffusion. This is a direct consequence of using a highly concentrated buffer solution as a catholyte causing a concentration gradient across the membrane. Furthermore, when a low current is present, a superimposed migration process occurs, attractive electrostatic forces act upon the charge carriers and drag them towards the anode. By increasing the current density in powered operation, this mechanism becomes dominant.

In the observed time frame, a successive ion exchange of the membrane is represented by an attenuated ion cross-over from the anolytic to the catholytic compartment. The overall ion transport is compensated by buffer cations permeating into the anolytic compartment due to backdiffusion. As the ion exchange capacity of the PEM is limited for the given geometry, it can easily be exhausted by high ion concentrations in hard water. In order to evaluate ion diffusion, it is thus indicated to compare the powered and stand-by operation of the PEM electrolyser (see Fig. 5).

As previously indicated in Fig. 4(a) for all four ions under investigation, the total ion transport depicted in Fig. 5(a) shows an approximate linear correlation (all $R^2 > 0.99$) with experimental time, independent of water hardness. However, a different picture can be drawn when the stand-by operation is closely looked at (Fig. 5(b)). We observe a delayed onset of the ion transport which differs dramatically from the ideal linear behaviour, especially for soft and medium water. This can be recognized most prominently for magnesium, as e.g. in soft water this ion species could only be detected in the catholyte after 4 h have passed. Its breakthrough time decreases with increasing water hardness level, indicating a successive ion exchange of the PEM. In the case of hard water, these effects are barely noticeable as the retardation time is limited to a minimum, thus allowing to describe the overall ion permeation process by a linear function, analogous to powered operation.

The retarded onset in stand-by operation might be due to a more stable Mg^{2+} -NafionTM interaction caused by the hydration sphere of the elements involved [59,60], hence leading to a delayed transport through the PEM. For the given geometry, the ion exchange capacity of the PEM equals 1.22 mEq [61], which offers sufficient capacities to temporarily delay Mg^{2+} diffusion. However, this effect becomes negligible under electrolysis conditions.

3.3. Batch-like operation in stagnant feed water

In various applications, pipe systems for tap water are not regularly flushed and are consequently prone to the formation and accumulation of pathogens which may pose a potential health threat [62,63]. To draw potable water on demand at any given point, it is necessary to continuously sanitize stagnant water storage or line systems. This corresponds to a batch-like treatment of defined water volumes which can be performed using an ozone-evolving PEM electrolyser setup as presented in this study.

Since the transport of hydrated cations leads to an increase in water volume of the catholyte, it is necessary to characterise the influence of the responsible charge carriers. When operating a PEM electrolyser in tap water, a rapid change in pH value of both catholyte and anolyte can be noted (see Fig. 6), which affects the SMEA performance [64,65]. After only 2 h of operation in a closed system, the anolytic pH value has dropped below 3 while the pH value of the catholyte has increased to 10. When a buffer is used in the catholytic compartment, the pH value of the catholyte remains constant during both stand-by and powered operation as long as the buffer capacity is sufficient.

During powered operation the cathodic H_2 evolution is supplied by protons permeating from the anolytic compartment through the PEM. However, if an unsufficient amount of H^+ ions is transported due to the presence of additional charge carriers (e.g. Na⁺), the equivalent shortage in protons is overcome by additional cathodic water splitting, leading to an accumulation of OH⁻ anions in the catholyte.

In an open sytem, ultrapure water slowly acidifies due to successive CO_2 dissolution which was partially reduced by argon purging. In standby operation, this could be observed for both anolyte and catholyte. However, once the electrolyser is in powered operation, this effect becomes negligible as the change in pH value increases dramatically due to additional ion permeation.

Comparing stand-by and powered operation, it can be noted that the total ion permeation differs by a much lower quantity than expected for a 100-times increased current density. Considering the aforementioned concentration gradient in the present setup, it is indicated that diffusion is the dominating process at low current densities. Transported cations diffusing from the membrane into the catholyte will exchange with available positive charge carriers across the entire PEM surface. While in buffered systems this can be due to (dissociating) buffer ions, ultrapure



Fig. 5. Total ion transport as a function of the experimental time. Normalization has been performed regarding the total ion concentration after 8 h of the respective experiments to allow for an identification of ion discrimination. **(a)** During powered operation of the electrolyser, a linear transport behaviour can be observed independent of water hardness. **(b)** In contrast to that, during stand-by operation, the total ion transport from the anolytic to the catholytic compartment is delayed. This is especially prominent for magnesium, which is held back for shorter periods of time with increasing water hardness levels (dotted lines).



Fig. 6. During electrolysis, the pH values within the anolytic and catholytic compartments diverge adversatively from their respective starting values when charge carriers apart from protons in ultrapure water (UPW) are present in tap water (top). When using a catholytically buffered system and medium water, an anolytical acidification is observed in both electrolysis and stand-by operation (bottom). In addition, ion permeation can be observed in both experiments.

water requires proton liberation, i.e. by autoprotolysis.

So far it has been shown that the permeation of ions occurs during both powered and stand-by operation of a PEM electrolyser with the given setup. Yet, the transport of any charge carrier apart from H⁺ through the PEM (denoted $\sum n_{ion, eq}$ for Na⁺, K⁺, Mg²⁺ and Ca²⁺) leads to a loss in H⁺ transport effectiveness, represented by its current share χ_{H^+} (eq. (4)) [66,67]. In operation, a value close to 100% is desired as this means that only a minimal amount of hardeners is transported across the PEM, influencing both the pH value and the active surface area of the electrodes.

$$\chi_{H^+} = 1 - \left(\frac{\sum n_{ion,eq} \cdot F}{I \cdot t}\right) \tag{4}$$

For all water hardness levels and current densities in powered operation, the observed current shares are depicted in Fig. 7.

Even in hard tap water, protons constitute the vast majority of ionic conductors due to their anodic generation according to eq. (1) and (2). This justifies the previous observations in section 3.1 that no significant influence of different charge carriers on water transport was found. It becomes apparent that with increasing current density, the current share for H⁺ transport approaches a maximum close to 100% which would equal an ideal electrolyte. The most efficient operation setting could be observed for soft water applying the highest current density J = 1.25 A cm⁻² with a current share of 99.4 ± 0.1%. In contrast to that, when applying low current densities and using hard water, the permeation-induced loss in χ_{H^+} led to values of only 93.5 ± 0.4%. The data shows that the effect of actual water hardness can partially be compensated by increasing the current density.

3.4. Formation of precipitates and mitigation of ion permeation

If a PEM tap water electrolyser is operated in a non-buffered system, the observed pH gradient is accompanied by permeation of tap water cations, which infiltrate the catholyte and are likely to form insoluble compounds under the developing alkaline conditions. In Fig. 8 the



Fig. 7. H⁺ transport-related current share χ_{H^+} of the electrolysis cell for different current densities and water hardness levels. When hard water is used, permeating ions affect the current share the most. The application of high currents partially compensates for that effect.

catholytic formation of precipitates during long-term operation is depicted.

Before electrolysis operation in tap water, the freshly installed titanium electrodes (Fig. 8(a)) show a shiny, porous surface without any visual contaminations, which is confirmed by EDX measurements. After 500 h of operation in hard water, the electrodes are covered with a white coating (Fig. 8(b)) which could not be observed during buffered operation. For post-operational investigations, the electrodes were recollected and reveal that the layer of scale (Fig. 8(c)) contains both magnesium and calcium, with the latter being found predominantly on the outer regions of the electrode. As the oppositely positioned anodes



Fig. 8. (a) Top view on the cathodic PEM contacting site **before** its usage in the electrolyser (non-buffered operation). Optical imaging (left) and SEM-EDX elemental mapping (right) show the absence of scaling. (b) Pre- (left) and post-operation (right), the catholytic compartment shows significant build-up of scale on the cathodes. (c) Top view on the cathodic PEM contacting site **after** its usage in the electrolyser (non-buffered operation). Optical imaging (left) and SEM-EDX elemental mapping (right) show the presence of scaling and enrichment of calcium and magnesium in areas affected by scaling. (d) XRF spectra of the pre- (red dashed lines) and post-operational (solid black line) cathodes. Signals related to the elements of interest are highlighted. (e) Diffraction pattern of the cathodic scale with signals assigned to the identified crystalline phases (\blacktriangle = Aragonite, β -CaCO₃; \textcircled = Calcite, λ -CaCO₃; \blacksquare = Portlandite, Ca(OH)₂; \checkmark = Brucite, Mg(OH)₂). The detail picture illustrates the relative scale composition.

are smaller in diameter, there is a defined center region where both the electric field as well as the ionic flux are expected to be the highest and where titanium signals are detected most prominently, hence indicating a nearly uncovered cathode surface. Scale formation and build-up between the cathode/PEM interface could result in a decreasingly available contact area, leading to higher local current densities which may eventually cause membrane stress and failure. A comparison of the preand post-operational XRF spectra of the cathodes (Fig. 8(d)) emphasizes the layered precipitate formation on the electrode surface, as titanium signals partially disappear whereas signals related to the hardeners emerge. XRD measurements (Fig. 8(e)) indicate that nearly all signals can be explained with the presence of hydroxides and carbonates of magnesium and calcium, namely Aragonite (β-CaCO₃), Calcite $(\lambda$ -CaCO₃), Portlandite (Ca(OH)₂) and Brucite (Mg(OH)₂). An approximation of the relative composition was performed using Rietveld refinement [68]. As both detected calcium carbonate allotropes make up for roughly 75% of the scale, the absorption of CO₂ and subsequent dissolution and carbonatization in the catholyte under unbuffered conditions must be considered.

An approach to mitigate ion permeation is the introduction of an auxiliary cathode within the analytic, ozone-evolving compartment. In order to assess its influence, ion permeation is evaluated for experiments with the auxiliary cathode connected to and disconnected from negative potential (Fig. 9).

With the auxiliary cathode connected, a mean current of I = 42 \pm 11 mA could be measured between the anode and the auxiliary cathode, which equals 3 \pm 1% of the total current applied. Using this modified operation mode, a decrease in total ion permeation of 18 \pm 4% was found without preference for any cationic species involved. As the applied current remained unchanged, an equal amount of anodically produced ozone can be expected. At every point during the experiments, the total ion permeation values that differ by their respective margins of error.

Consequently, the auxiliary cathode appears to introduce an electric field that is opposed to the field caused during powered operation of the PEM electrolyser. Ions are therefore less attracted to the anode/PEM interface and can be expected to cause a less prominent pH gradient across the membrane during batch-like operation, eventually leading to a reduced risk of precipitation in the catholytic compartment and thus increase the expected lifetime of the electrolyser setup.



Fig. 9. Cumulated ion permeation as a function of the experimental time, normalized to its highest total value. Error bars referring to the summed-up ion permeation result from the propagation of uncertainty for each ion permeation involved. During both operational modes under standard conditions, ion permeation increases monotonously. A mean and indiscriminate permeation suppression of $18 \pm 4\%$ was determined.

4. Conclusion

In the present work, a specific PEM electrolyser setup for ozone evolution is characterised during its application as a tap water electrolyser. Both ion and water transport were modeled for different water hardness levels and current densities representing varying performance requirements for ozone evolution. During operation, a significant water transport of 95 \pm 2 mmol A⁻¹ h⁻¹ from the analyte to the catholyte can be noticed which is directly proportionate to the applied current and needs to be considered for scaled-up applications. The water transport was found to be decoupled from the ion permeation. The latter also takes place in stand-by operation and increases with an elevated water hardness level of the anolytic feed as well as with current density. The transport of ions correlates with their ion mobility in water, leading to the conclusion that their transport to the anode/PEM interface is limited. Especially for a batch-like operation e.g. in a stagnant water, a high proton efficiency is desired and can be achieved by the application of increased current density. As carbonates make up for about 75% of the cathodic scale, the dosing of an acidic buffer is recommended to ensure long-term stability of the SMEA. Thus, this technique can be applied in regions with soft tap water, without requiring any further preprocessing of the water feed. However, as hard feed water is related to a higher risk of precipitations, the use of an upstream water softening unit can be recommended. Furthermore, an auxiliary cathode can be used to suppress ion permeation by nearly 20%.

The obtained models allow for a differentiated ion and water transport assessment during tap water electrolysis of any water quality. Future studies can improve by focusing on the influence of tap water ions on the efficiency of electrochemical ozone evolution and consider the anodic treatment of anions to allow for an even more comprehensive insight into tap water electrolysis employing a structured PEM electrolyser.

CRediT authorship contribution statement

Roman Grimmig: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Visualization, Writing – original draft. **Philipp Gillemot:** Conceptualization, Methodology, Formal analysis, Data curation, Visualization, Writing – original draft. **Samuel Stucki:** Conceptualization, Writing – review & editing. **Klaus Günther:** Supervision, Writing – review & editing. **Helmut Baltruschat:** Supervision, Writing – review & editing. **Steffen Witzleben:** Funding acquisition, Resources, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Conflicts of Interest

Samuel Stucki works as scientific consultant for Innovatec Gerätetechnik GmbH which provided resources for the present study. All other authors declare no conflict of interest.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2022.121063.

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