A novel method for Ion Exchange Capacity characterization applied to Anion Exchange Membranes for Water Electrolysers

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Abstract. Hydrogen production from water electrolysis, hydrogen fuel cells and redox flow batteries are the right approach for the renewable energy sector because the electricity generated by solar, wind, photovoltaic, hydroelectric can be managed with a carbon-free approach. These technologies all have in common one fundamental component: the membrane. Different types of membranes have been developed for both cationic and anionic exchange, and recently, research activity focalized on improving their performances is very fervent. One fundamental characteristic of a membrane is its Ion Exchange Capacity (IEC), i.e. the density of charged functionalizing groups. Within our research project NEMESI, funded by EU-PNRR (ID: RSH2B_000002), and dedicated to Anion Exchange Membrane Water Electrolysis, we studied and validated a novel alternative method to measure IEC. The present titration methods have limitations for the need of dedicated hardware or qualitative inspection of their color-turning endpoint. The proposed method, based on the redox titration of potassium ferricyanide with ascorbic acid, allows a quantitative and independent assessment based on both potentiometric and spectrophotometric measurements, along with the usually adopted visual observation, as the yellow-colored ferricyanide is reduced to colorless ferrocyanide. Moreover, if compared to the classical Mohr titration with silver nitrate, the new method can be carried out at variable ferricyanide concentrations during the addition of the ascorbic acid, so a complete curve of the redox reaction can be constructed: the initial ferricyanide ion load of the membrane (IEC) can thus be derived in a more precise way than with a single-point evaluation. Only one Ag/AgCl reference electrode and a platinum working electrode are required without any power supply/potentiostat. The proposed method was validated using Anion Exchange Membranes with known IEC.

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1 Determination of Ionic Exchange Capacity of a membrane

Anion Exchange Membranes (AEM) are ion-conducting functionalized separators widely used in several technologies, such as alkaline electrolizers, fuel cells, redox flow batteries and even electrodialysis. While providing insulation against electrical current leakages and compartmentation of process gases, they ensure a good ionic conductance thanks to their functionalization with charged ionomer. The functionalization with positively charged groups provides a much higher concentration of anions inside the membrane than in the bulk of the electrolyte solution and thus an enhanced ionic (anionic) conductivity. The Ion Exchange Capacity (IEC), i.e. the loading of charged groups per unit weight of the membrane, is one of the most important properties of the membrane since it is proportional to the membrane ionic conductivity and hence closely related to performance.

The assessment of a membrane's IEC is normally carried out with Mohr [1] or acid-base titration [2]. These methods rely on dedicated hardware or alternatively on a qualitative evaluation of the color-turning endpoint of titration with indicators such as potassium chromate (Mohr) or phenolphthalein (acid-base). Systematic errors, like the residual presence of chlorides in low-quality deionized water or carbonate contamination after CO_2 takeup also affect the measurements. Alternatively, some producers assess the IEC of Anion Exchange Membranes with (expensive) NMR spectroscopy and provide ranges of IEC normally affected by important spreads [3]; these values refer to new membranes at their beginning of life, while it would be interesting for a user to evaluate the membrane IEC after operation.

Here we propose an assessment of an IEC of an AEM membrane with a novel technique based on the membrane's ion exchange with potassium ferricyanide ($K_3Fe(CN)_6$). After a preliminary activation bath in a high concentrated solution of $K_3Fe(CN)_6$, the membrane is moved to a second solution (potassium phosphate buffer) where it releases the ferricyanide absorbed in the first bath. The content of ferricyanide in this solution is then assessed, providing an estimate for the ion takeup capability of the membrane.

The advantage of this method over similar techniques evaluating the membrane's ion exchange with chloride ions or hydroxide ions is that the ferricyanide content of a solution can be easily assessed in three ways [4], with two of them quantitative:

1- VISUAL ASSESSMENT OF THE TITRATION TURNING POINT: Ferricyanide is reduced to ferrocyanide ($K_3Fe(CN)_6 + e^- \rightarrow K_4Fe(CN)_6$) by a reducing agent such as ascorbic acid, added step by step with a titration procedure. Since ferricyanide is bright yellow while ferrocyanide is transparent, the color-to-colorless transition after the addition of a known amount of ascorbic acid allows the assessment of the initial ferricyanide concentration.

2- SPECTROPHOTOMETRIC MEASUREMENT: Ferricyanide solutions have a very well characterized visible light absorbance and a narrow absorption peak at the wavelength of 420nm [5]. Absorbance scales with the ferricyanide concentration and provides a very precise assessment of the latter. This method could not be applied to chloride determination in Mohr method, since AgCl precipitates are opaque and light-reflecting.

3- POTENTIOMENTRIC ASSESSMENT: The equilibrium potential of the ferricyanide-ferrocyanide redox reaction follows the ferricyanide concentration according to the Nernst equation. The evaluation of this potential on a platinum working electrode with respect to a reference Ag/AgCl electrode provides a precise assessment of ferricyanide concentration.

2 Membrane assessment

A 5cmx5cm AF3-HWK9-75-X AEM Ionomr® membrane, sold in original chloride and iodide form, was soaked in a thermostated 35°C preactivation bath of 200ml of 0.2M potassium ferrycianide for 6h. This preliminary bath is expected to exchange (a good part of) the original iodide and chloride content of the membrane with ferricyanide ions.
The use of a preliminary activation bath with refreshing of the solution before the activation bath is a general practice recommended by the vendor. One of the reasons is to keep the membrane always exposed to a "fresh" solution with a minimal bulk content of chlorides and iodides in such a way that the release of these ions from the membrane is promoted. The second reason is that iodide ions, originally present at high concentration in the membrane, can in principle react and reduce ferricyanide ions to ferrocyanide. The replacement with a new "fresh" solution avoids (or limits) the contamination of the ferricyanide bath with ferrocyanide, which may affect the following potentiometric determination.
After 6h, the preactivation bath dramatically darkened in color: this behavior was attributed to the release of iodide ions from the membrane to the solution and their oxidation to triiodide I_3^- ions. The membrane was then moved to the activation bath of 0.7M potassium ferricyanide at ambient temperature, where it was kept for 48h in the dark.
The original preactivation solution was still observed for another 60h: blue shades appeared, attributed to a small amount of ferri-ferrocyanide $Fe_4[Fe(CN)_6]_3$ (Prussian Blue). The formation of Prussian Blue is a mark of instability of the ferricyanide solution in presence of reducing agents (iodide and chloride ions in this case) and acidic media (for the takeup of CO_2). The stability of potassium ferricyanide at neutral pH and in absence of reducing agents is instead well documented in literature [6-9].
This observation motivates the "sacrificial" pre-activation bath of lower concentration where reaction of ferricyanide with iodide and chloride ions eventually takes place (with consequent reduction of ferricyanide to ferrocyanide and formation of degradation products) followed by a "fresh" activation bath of higher ferricyanide concentration when the membrane has already released most of its potentially reactive iodide and chloride content: actually the color of the activation bath solution of 0.7M potassium ferricyanide after 48h was almost unchanged.
After the activation bath, the membrane had a yellow-reddish color and was dipped in four large beakers of deionized water for rinsing. The membrane was then moved to the test solution of 100ml of 2M potassium phosphate buffer (pH7) where it was kept for 24h for exchanging phosphate ions with ferricyanide ions. The test solution turned to a pale yellow color as the membrane released the ferricyanide ions formerly absorbed in the activation bath.
After 24h of ion exchange, the membrane was removed and the ferricyanide concentration in this test solution was assessed, as a measure of the Ion Exchange Capacity of the membrane.
Potentiometric and spectrophotometric assessments were performed on the same sample upon the progressive addition of 0.01M ascorbic acid (AA) in steps of 0.1ml (after a separate preliminary calibration with test solution of 1mM $K_3Fe(CN)_6$ reduced in steps of 0.5ml AA).
The ascorbic acid added to the test solution performs a redox reaction with the potassium ferricyanide:

$$C_6H_8O_6\ (AA) \rightarrow C_6H_6O_6\ (DHA) + 2H^+ + 2e^- \quad (1)$$

$$2\ K_3Fe(CN)_6 + 2e^- \rightarrow 2\ K_4Fe(CN)_6 \quad (2)$$

One mole of ascorbic acid (AA) upon oxidation to dehydroascorbic acid (DHA) releases two moles of electrons and two moles of H^+. The H^+ generated by the oxidation of ascorbic acid and by the dissociation of ascorbic acid to ascorbate are managed by the phosphate buffer which keeps the solution at constant pH. The electrons reduce two moles of ferricyanide to ferrocyanide for each mole of ascorbic acid added to the solution.
The role of pH stabilizer of the phosphate buffer is very important since ferricyanide may undergo degradation in acidic environment, with dangerous release of cyanide ions: the

solution must be kept at neutral pH at any time. The concentrated potassium phosphate buffer also works as a supporting electrolyte enhancing the ionic conductivity for the potentiometric measurement.

2.1 Spectrophotometric assessment

Hach DR6000 spectrophotometer is used to assess the absorbance of the sample at a wavelength of 420nm. At this wavelength, ferricyanide has the highest absorbance in the visible spectrum [5], while ferrocyanide is transparent. For our range of concentrations, absorbance is directly proportional to ferricyanide concentration according to Beer's law.

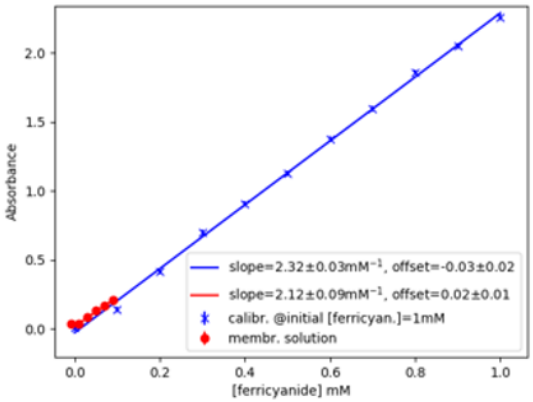

Fig. 1. Spectrophotometric assessment of absorbance as a function of ferricyanide concentration for the calibration solution with 1mM of initial $K_3Fe(CN)_6$ concentration (blue crosses) and the membrane solution (red dots). Concentrations decrease from right to left as long as ascorbic acid is added and $K_3Fe(CN)_6$ reduced to $K_4Fe(CN)_6$.

The absorbance as a function of ferricyanide concentration (Fig. 1) decreases from right to left as ascorbic acid is added and ferricyanide turned into ferrocyanide. The line slope follows the literature range [4,5] of 1.02-1.06 $mM^{-1}cm^{-1}$, considering a cuvette internal diameter of 2.1±0.1cm. The observed zero-absorbance point coincides with the turning point to transparent color (visual indication): for the calibration curve with 1mM of initial $K_3Fe(CN)_6$ concentration in 100ml, this happens for 5ml of added ascorbic acid (5ml x 0.01M = 0.05 mmol of AA reducing 0.1 mmol of $K_3Fe(CN)_6$). The initial ferricyanide concentration of the membrane solution derived from the fit is 0.0908 ± 0.0012mM, which corresponds to 0.0272(3) meq in 100ml of test solution. The vendor-rated IEC for our membrane sample, of dry weight 0.1935±0.0002g measured before activation, is 0.368meq minimum, which indicates that the tested protocol is able to exchange only 7.4% of the rated ionic content.

2.2 Potentiometric assessment

The open circuit voltage of a 5mm x 10mm Laborxing platinum mesh working electrode was measured against a 3M KCl Laborxing Ag/AgCl reference electrode with a Fluke 289 multimeter, for the different steps of ascorbic acid addition with magnetic stirring @400rpm. When plotted against the logarithm of the ratio of concentrations of ferrocyanide $[Fe(CN)_6]^{4-}$ vs. ferricyanide $[Fe(CN)_6]^{3-}$, the potential follows a linear trend described by a one-electron Nernst equation (Fig. 2):

$$V = V_0 - RT/F \ln([Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}) \quad (3)$$

Writing the ferrocyanide concentration as the initial ferricyanide molarity minus twice the (known) molarity of ascorbic acid added to the test solution, the fit has two free parameters: one is the initial ferricyanide concentration (the target of the assessment), the other is the standard reduction potential V_0. The amount of ascorbic acid added when the potential drops and becomes unstable ($[Fe(CN)_6]^{3-}\approx 0$ in eq.(3)) was 0.4ml-0.5ml, corresponding to 0.08-0.10mM of initial $[Fe(CN)_6]^{3-}$, in agreement with the photometric assessment. The calibration curve shows a logarithmic slope of ≈-1 in units of RT/F (one-electron reduction).

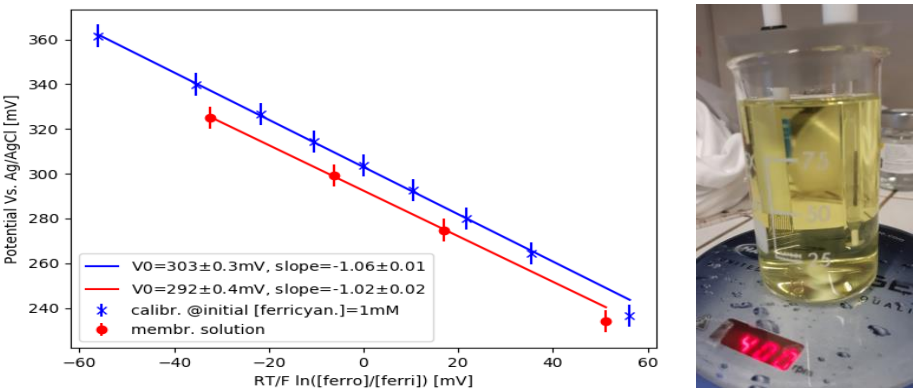

Fig. 2. Potentiometric assessment of the working electrode potential w.r.t. Ag/AgCl reference electrode: calibration curve for 1mM of initial ferricyanide concentration (crosses) vs. assessment of resulting membrane exchange solution (dots).

3 Assay with the "standard" method: Mohr titration

A 5cm x 5cm AF3-HWK9-75-X AEM Ionomr® membrane was soaked in a 200ml 1M KCl activation bath to promote full ion exchange to chloride form. After 24h the membrane was dipped four times in large volumes of deionized water and moved to an exchange bath of 250ml of 1M KNO_3 where it was kept for 24h to release chloride ions in the solution while absorbing nitrates. A Mohr-like procedure was then applied to detect the chloride content of this final solution. A small amount (0.08mM) of potassium ferricyanide was used as color indicator of the titration turning point, preferred for safety reasons to the standard K_2CrO_4. The progressive addition of 0.01M $AgNO_3$ in steps of 1ml induces the precipitation of AgCl: the yellow solution became more and more opaque for the white color of AgCl precipitates. When the full chloride content of the solution is consumed, silver ferricyanide starts to precipitate and the solution turns to orange (Fig. 3): this point was observed to occur between 31ml and 33ml of added AgNO3, corresponding to 0.31-0.33mmol of chloride ions.

Fig. 3. Color change after the qualitative Mohr titration: initial (yellow) color for the presence of $K_3Fe(CN)_6$ indicator, yellow-opaque color after precipitation of 0.1mmol of AgCl, yellow-to-orange turning point @33ml of added 0.01M $AgNO_3$ (circled) and orange color for the $Ag_3Fe(CN)_6$ precipitates.

4 Conclusion

Within the framework of the research project NEMESI, funded by EU-PNRR, we proposed a novel alternative method to measure the Ionic Exchange Capacity of a membrane, based on the evaluation of its ionic exchange with potassium ferricyanide. The amount of ferricyanide exchanged by the membrane can be measured with three methods (visual, spectrophotometric, potentiometric), with two of them quantitative.
The assessment of a AF3-HWK9-75-X AEM Ionomr® membrane produced a good signal (IEC=0.0272 ± 0.0003 meq for a dry weight of $0.1935 \pm_2$ g), consistent for the three methods, but able to reveal only a small fraction (≈7.4%) of the membrane IEC from the vendor datasheet. We attribute this outcome to an insufficient volume and concentration of the first activation bath, the large size of the $Fe(CN)6^{3-}$ ions (low diffusivity in the membrane), the rinse protocol between the activation and the exchange bath which eventually jeopardizes part of the ionic content. The removal of the rinse step, likely the most impacting factor, was observed to yield a 6x on the measured IEC. The (qualitative) outcome of the standard Mohr method is instead much closer to the IEC datasheet value. Although several aspects of the ferricyanide-based protocol can be improved (ion exchange to a higher temperature, frequent replacement of the activation bath to remove contaminants, higher concentration and soaking times, membrane drying between baths…) in order to detect the full ionic capacity of the membrane, our method can still be used as it is with a reference calibration curve, for instance to detect any IEC deterioration after operation, although with larger relative errors.
Compared to the assessment of the titration endpoint with the standard Mohr or acid-base methods, the introduced methodology may allow for a greater accuracy, which comes from the multiple-technique (visual, spectrophotometric, potentiometric), quantitative and multiple-point nature (linear fit of a line with varying ferricyanide concentrations instead of a single titration turning point). A survey of the typical precision range on IEC of the classical methods (from -50% to +10%) is available in Fig. 1 of [3].
Finally, our method avoids expensive chemicals or highly toxic indicators (such as $AgNO_3$ or K_2CrO_4 for Mohr), and/or expensive dedicated hardware. Potassium ferricyanide is cheap, relatively stable and safe when operated under neutral conditions: it is a very well characterized compound frequently used in graduate or undergraduate Chemistry courses. For these reasons the proposed ferricyanide method has the potential to complement the existing standards for the IEC determination.

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