Conductometric titration for analyzing perfluorosulfonic acid membranes

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Abstract

In this work the analythical technique, conductometric titration, is presented to determine the equivalent weight, the total exchange capacity or the dry weight capacity of the exchange polymeric material.

Some of the results obtained by the analysis of perfluorosulfonic acid (PFSA) membranes (Nafion® 115 and 117) under this technique were presented to show the procedure followed and to contrast them (the results) with those published by the manufacturer.

Background

One very important electrochemical property of ion exchange materials is the ion exchange capacity. This property is the measure of the number of fixed charges per unit weight of dry polymer.

In practice, this property is determined by titration of the ions fixed using NaOH or HCl depending on the cationic or anionic capacity of the material. The first step of the procedure consists of equilibrating the material with NaOH or HCl for 24 hs. Then, the sodium or chloride has to be eliminated rinsing it with distilled water during another 24 hs. Just at this point, the material is in conditions to evaluate the ion exchange capacity by back titration using methyl orange as indicator and 1 M NaOH or 1 M HCl, as titrant. So, approximately 50 hours are necessary to determine its value. In this work the conductometric titration is presented as a promising technique for the determination of this parameter, reducing time considerably.

Through the graphical representation of conductivity, as a function of the volume of titrant added, which consists of two straight lines that intersect at the equivalent point, it is possible to obtain the volume of titrant needed to complete the reaction proposed between the polymer and the titrant: exchange or neutralization.

Neutralization reaction:

$$RSO_3H + NaOH \rightarrow RSO_3Na + H_2O$$

Ionic exchange reaction:

$$RSO_3H + NaCl \rightarrow RSO_3Na + HCl.$$

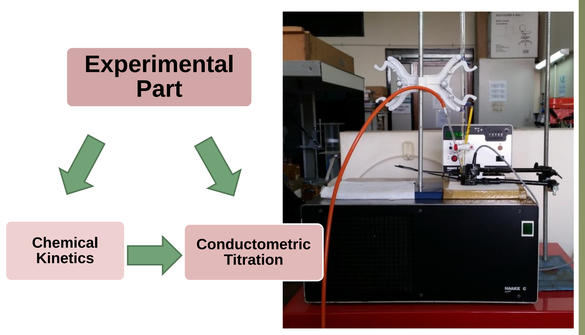
Methods

Kinetic study

1. Determine the weight of the sample of Nafion® membrane.
2. Calculate the volume needed to exchange all the exchangeable ions.
3. Add 70 mL of distilled water and the volume calculated in (2) into a pyrex beaker.
4. Stir the solution for 50 minutes, using a magnetic stirrer.
5. Introduce the pyrex beaker into a thermostat until the working temperature of 19°C ± 0.1 is reached (50 minutes).
6. Place the conductivity meter and the nitrogen bubble stirring system into the pyrex beaker.
7. Submerge the sample of Nafion® membrane into the system in the pyrex beaker.
8. Record the conductivity once a minute over 90 minutes.

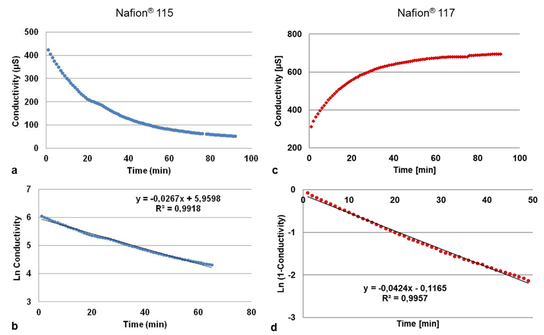
Conductometric titration

1. Determine the weight of the sample of Nafion® membrane.
2. Calculate the volume needed to exchange all the exchangeable ions.
3. Add 70 mL of distilled water and the sample of Nafion® membrane into a pyrex beaker.
4. Introduce the pyrex beaker into a thermostat until the working temperature of 19° C ± 0.1 is reached (50 minutes).
5. Place the conductivity meter and the nitrogen bubble stirring system into the pyrex beaker.
6. Add fixed volumes of titrant through a burette after pre-determined periods of time (half-life periods).
7. Once each period has elapsed, the system conductivity has to be measured and recorded.



Results

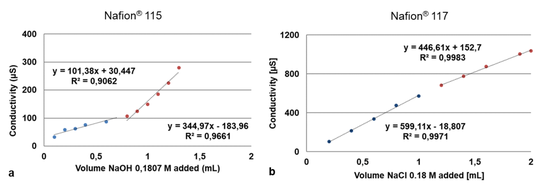
Kinetic study



Graphical representations of (a) and (c) conductivity as a function of time and (b) and (d) equation velocity applied to the conductivity measurements as a function of time.

Sample	Rate constant (min–1)	Half life period (min)
Nafion® 115	0.0267	26
Nafion® 117	0.0424	16

Conductometric titration



Conductometric titration by the addition of titrant every (a) 26 minutes and (b) 16 minutes.

Sample	Weight (g)	Total Acid Capacity (meq/g)	Ion Exchange Capacity (meq/g)
Nafion® 115	0,1521	0,95-1,01	1,05
Nafion® 117	0,2133	0,95-1,01	1,12

Conclusions

- Study of the kinetics allows calculating the half life period which abruptly reduces the long period of time that needs to be waited in titration.
- Accuracy and simplicity of operation.
- It is not necessary to use an indicator. This has two benefits: Not incorporating a contaminant into the system and the value of the determination error as a consequence of the wide range of pH that it presents.
- The time needed to carry out the complete determination is reduced (in this particular case, 8 hours instead of 50).

References

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Any question?
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