

### Electrogravimetric Methods: an Attractive Tool for Investigating Solid Electrolytes for Electrochemical Conversion Devices

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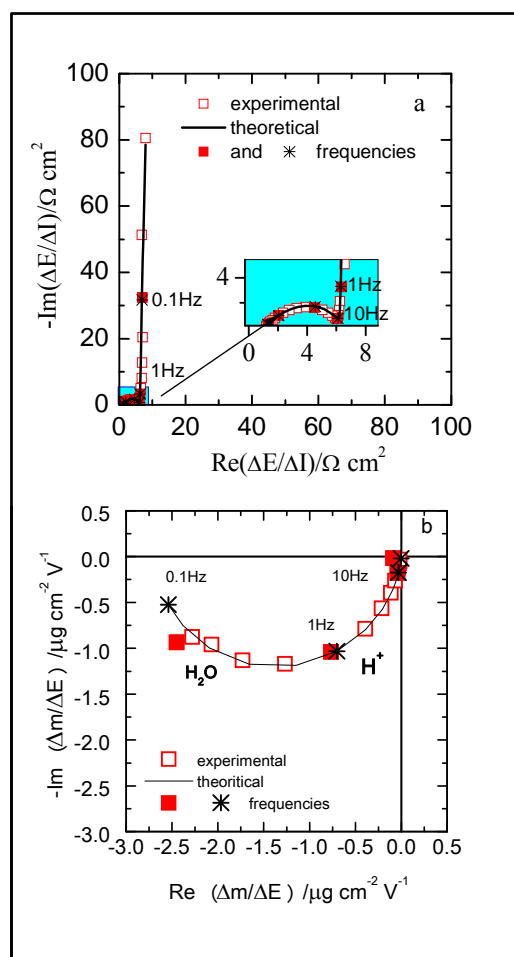
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The need for new solid electrolytes with improved ion-conducting properties continues to be one of the main pressing concerns in fuel cell research. In accompanying this search for optimal materials, appropriate characterization tools to assess key parameters of newly developed solid electrolytes are required. This tutorial paper will focus on electrochemical impedance spectroscopy (EIS), which has been established as a powerful technique in the characterization of electrochemical conversion devices such as fuel cells.<sup>1</sup>

Further attention will focus on coupling EIS with gravimetric methods (fast quartz crystal microbalance (QCM)) under dynamic regime. This coupling, so called *ac*-electrogravimetry measures the usual electrochemical impedance,  $\Delta E/\Delta I$  ( $\omega$ ), and the mass/potential transfer function,  $\Delta m/\Delta E$  ( $\omega$ ), simultaneously.<sup>2-4</sup> The main interests of this coupling are its ability to indicate the contribution of the charged and uncharged species and to separate the anionic, cationic, and free solvent contributions during the electrochemical/chemical processes. These features make the *ac*-electrogravimetry an attractive and appropriate tool to investigate transfer/transport phenomena of charged and uncharged species in ion-conducting membranes/electrolytes.

As a pertinent example, the adaptation of *ac*-electrogravimetry to evaluate the  $H^+$  diffusion and insertion in polymer electrolyte membranes (PEMs) will be discussed.<sup>5,6</sup> The species that are essentially not easy to detect gravimetrically, such as protons, could be studied due to the high precision and sensitivity of these coupled techniques. To perform such experiments, an electroactive film mediator has to be inserted between the working electrode of the microbalance and the proton conducting membrane. This mixed conductor mediator is necessary to provide transfer of protons between the different interfaces and therefore, to study the proton transport inside PEMs which are only ionic conductors. The results of a new class of hybrid membranes (HMs) based on a fluorinated polymer associated with mesostructured silica (Fig. 1) will be compared to model materials such as perfluorosulfonic acid based membranes (PFSA). An original theoretical approach will be discussed for extracting the key parameters (such as concentration change of the exchanged species and the diffusion coefficient of the protons in PEMs) from coupled EIS and QCM data. The characterization of new membranes with these novel techniques can explain the ion conduction behavior and can determine whether the limiting mechanism, if there is any, is the proton insertion or diffusion. By evaluating the potential of these new materials via coupled EIS methods, specific materials can be effectively and quickly chosen based on their properties.



**Fig. 1** Measured (scatters) and calculated (line) for the different transfer functions: a.  $\Delta E/\Delta I$  ( $\omega$ ) and b.  $\Delta m/\Delta E$  ( $\omega$ ) of the hybrid membrane/mediator film bilayer immersed in 0.5 M  $HClO_4$  at 0.2 V/SCE.

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