

Electrical impedance spectroscopy characterisation of supported ionic liquid membranes

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Abstract

Supported liquid membranes (SLMs), prepared by immobilising the room temperature ionic liquids (RTILs) $[C_n\text{MIM}]\text{PF}_6$ ($n=4$ and 8) and $[C_{10}\text{MIM}]\text{BF}_4$ in a polyvinylidene (PVDF) supporting membrane, were prepared and characterised by electrochemical impedance spectroscopy (IS). This non-invasive technique allows the determination of the electrical properties of a given sample, such as the electrical resistance and capacitance under working conditions, i.e., in contact with saline solutions.

Bearing in mind that the water content of the ionic liquids can drastically affect their physicochemical properties, impedance measurements of the SLMs, placed between two aqueous solutions, were carried out at regular time intervals, in order to assess the impact of the presence of water inside the RTILs on the electrical properties of supported ionic liquid membranes. The electrical resistance of the SLMs and its variation during long-term operation was also used as a physical parameter to identify the presence/loss of ionic liquid from the pores of the support. Additionally, the comparison of the IS results obtained for the SLMs with those obtained for the supporting membrane was carried out, in order to gather information about electrical changes associated with the presence of ionic liquid in the pores.

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1. Introduction

Room temperature ionic liquids (RTILs) are air and water stable salts, composed of an organic cation and either an organic or an inorganic anion. In recent years, RTILs, especially those based upon the 1-*n*-alkyl-3-methylimidazolium cation ($[C_n\text{MIM}]^+$), have been the object of ever-growing research interest [1,2]. Because they have a non-measurable vapour pressure and are able to solvate a large variety of organic and inorganic species, RTILs are emerging as alternative green solvents, namely as reaction media for synthesis, catalysis and biocatalysis [3–5]. The non-measurable vapour pressure of RTILs, combined with their non-flammability,

liquidity over a wide temperature range, relatively broad electrochemical window, high ionic mobility and good electrical conductivity [6,7] has also prompted their utilization as electrolyte solutions in fuel cells, solar cells and capacitors [8–10]. Additionally, their limited solubility with various solvents, including water, has made their use very attractive as organic phase in supported liquid membranes (SLMs) in order to obtain stable SLMs [11], namely for gas–gas and gas–liquid separations [12].

Recently, we evaluated the potential of using SLMs with ionic liquids for selective solute separation. The observation that water possesses a measurable solubility in the $[C_n\text{MIM}]$ RTILs led us to investigate the mechanisms involved in the solubilisation and transport of water through the corresponding SLMs [13]. The effect of water mobility on the mechanism of solute transport between aqueous phases, when

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separated by a SLM with ionic liquids and the evaluation of the SLMs stability by X-ray photoelectron spectroscopy (XPS) were also addressed [14,15]. The XPS and stability studies showed that there was no observable ionic liquid displacement from the membrane pores [15]. Solute transport, between two aqueous environments, was found to be mainly regulated, in an initial period, by the solute affinity towards the ionic liquid. However, in the course of the experiment, water was taken up by the membrane and water microenvironments were formed. As a result, solute transport through these water microenvironments became the dominant mechanism, leading to a deterioration of the membrane performance over time [13,14].

The present work seeks to broaden the field of application of supported ionic liquid membranes, taking advantage of the excellent conducting properties of ionic liquids. A thorough characterisation of the electrical behaviour of supported ionic liquid membranes constitutes therefore an essential step to evaluate their ability to transport charged species and their potential utilisation in electrochemical applications.

Impedance spectroscopy (IS), a non-destructive technique, will be used to determine the electrical properties of the supported ionic liquid membranes, such as the electrical resistance and capacitance under working conditions, i.e., in contact with saline solutions. This technique was recently used to electrically characterize the supported liquid membrane obtained by immobilising a phenylphosphonate uranyl solution (UPP) in a porous commercial alumina membrane support (Anopore) [16]. The electrical resistance of the modified membrane was used as a physical parameter to identify the presence/loss of the UPP solution from the pores of the support.

Bearing in mind that the water content of a given ionic liquid can drastically affect its properties (e.g. density and viscosity) [13,17,18] and that, among other parameters, viscosity has been reported to have a significant effect on the ionic liquids' conductivity [19], we started by evaluating the effect of the water content on the electrical properties of the RTILs tested.

Impedance spectroscopy measurements of the SLMs, placed between two aqueous solutions, were carried out at regular time intervals to understand the impact of the presence of water microenvironments on the electrical properties of the SLMs. The comparison of the SLM impedance results before and after its contact with the surrounding aqueous solutions will also be used as a tool to verify the retention of ionic liquid in the pores, after operation. If the ionic liquid is displaced from the pores of the supporting membrane, the pores will be filled with the electrolyte solution (NaCl, which has a lower conductivity), thus leading to an increase in the electrical resistance of the system.

The IS results obtained for the SLMs will be compared with those of the supporting membrane, in order to obtain information about electrical changes associated with the presence of ionic liquid in the pores. Additionally, the comparison of the electrical response of the SLMs with that of a typically

proton conducting membrane, such as Nafion 117, will be carried out.

2. Theoretical background

Impedance measurements were carried out by applying an alternating voltage, in a wide range of frequencies, to an electrochemical cell and by measuring the resulting electric current. The voltage applied (v) is a sine wave input, varying with time (t), defined as

$$v(t) = V_0 \sin(\omega t) \quad (1)$$

where V_0 is the maximum voltage intensity and ω is the angular frequency. The resulting electric current (i) is also a sine wave:

$$i(t) = I_0 \sin(\omega t + \phi) \quad (2)$$

where I_0 is the maximum current intensity and ϕ is the phase angle between the applied voltage and the current intensity. The electrical impedance, $Z(\omega)$, defined as the ratio between the applied voltage and the resulting electric current, $Z(\omega) = v(t)/i(t)$, is expressed as

$$Z(\omega) = Z_{\text{real}} + jZ_{\text{img}} \quad (3)$$

where Z_{real} is the real part of the electrical impedance and Z_{img} is the imaginary one. The analysis of the impedance experimental data obtained $Z(\omega)$ can be carried out by the complex plane Z^* method, plotting the impedance imaginary part ($-Z_{\text{img}}$) versus the real part (Z_{real}) in a diagram called a Nyquist plot.

If the system behaves like a parallel resistance–condenser (RC) circuit, the impedance has both resistive and capacitive components, and it is possible to fit the equation for the parallel RC circuit to the impedance experimental data. In that case, the Nyquist plot looks like a semicircle in the Z^* plan, which intercepts the Z_{real} -axis at R_∞ ($\omega \rightarrow \infty$) and R_0 ($\omega \rightarrow 0$). The resistance of the system, R is given by $(R_0 - R_\infty)$. The maximum of the semicircle is equal to $0.5 \times (R_0 - R_\infty)$ and occurs at frequency $\omega = 1/RC$, where R is the resistance, C the capacitance and the product (RC) is the relaxation time [20,21]. The resistance and capacitance can be used to electrically characterize a given material or system. If the system is complex and involves two subsystems with different dielectric properties, two different relaxation processes may appear in the Nyquist plot, and the equivalent circuit for the entire system is a series association of two RC elements, one for each sub-system [20,21].

3. Experimental

3.1. Materials

The room temperature ionic liquids (RTIL) used in this study, prepared following reported procedures [22–24], were:

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