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Composite sPEEK membranes for vanadium redox batteries application

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Introduction. Vanadium redox batteries (VRBs) have received a strong attention as environmental friendly and high efficiency power sources. The polymeric proton exchange membrane is a key component of this typology of batteries, which must have high ion exchange capacity, a good proton conduction, chemical stability and a low permeability to vanadium ions. One of the most investigated membranes having a high proton conductivity and a good chemical stability consists in Nafion, but its vanadium ions permeability is still too high for a real application[1,2]. Recently, different approaches have been pursued to tailor the suitable ion exchange component for this application, such as the development of aromatic thermostable polymers[3] and blends of polymers. Indeed, these membranes, nevertheless show a lower proton conductivity than Nafion, they provide a lower permeability to vanadium ions and, consequently, an increased selectivity. In this work, sulphonated PEEK composite membranes, containing different weight percentages of a functionalised silica, were prepared, investigated and compared to the pristine polymers.

Experimental

The sulphonated PEEK based membranes (s-PEEK) were prepared starting from a Polyetheretherketone with two different sulphonation degrees (50% and 64%DS)[4]. A percentage ranging 0-20%wt/wt of functionalised silica (3-aminopropyl-functionalised silica) was used for the composite membranes preparation.

The following characterisations were carried out on all prepared membranes: Ion Exchange Capacity (IEC) was measured through an acid-base titration[4]; Vanadium Uptake (Vup%) was calculated by the difference in weight of a dried and wet sample according to the formula:

$$Vup, \% = [(m_{wet} - m_{dry}) / m_{dry}] \times 100$$

in which m_{wet} was measured after immersion in a $VOSO_4$ 1M in a H_2SO_4 2M solution at room temperature for 24 hrs and m_{dry} by drying the sample in a vacuum oven at 80°C for 2 hrs; proton conductivity (sigma) was measured in the longitudinal direction at 30°C and full humidification (100% RH)[4]. An important parameter to be investigated is the Vanadium ions permeability (P). The experimental apparatus consists in two flasks[5] of 610 ml, the first containing a 1M $MgSO_4$ in 2M H_2SO_4 solution as a reference and the other one containing a 1M $VOSO_4$ in 2M H_2SO_4 solution, respectively. A membrane sample of (3.14 cm^2) is placed between two different solutions. The measurements were performed at room temperature and aliquots of 10 ml from the flask containing the $MgSO_4$ solution were taken at different times. The concentrations of these solutions were spectrophotometrically measured using an UV/VIS device. The selectivity parameter (phi) was calculated as the ratio between proton conductivity and vanadium permeability.

Results and Discussion

The obtained chemical-physical results are reported in fig. 1 a-b. IEC of sPEEK membranes decreases with the introduction of filler, except for the sample sPEEK64-10, which is similar to bare polymer membrane (sPEEK64-0). This behaviour could be explained considering the dual

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contribution of this kind of filler: the first consists in the inert nature of silica, which does not possess own exchangeable protons, the second in the amino groups presence interacting with the sulphonic groups of the polymer inhibiting the exchange capacity of the involved protons[4]. The effect of sulphonation degree is evident in Vup measurements (Fig.1b). In fact, composite membranes having a 64%DS show an higher Vup than the bare one, while a different trend is highlighted for a 50%DS. The different behaviour could be associated to a compromise between the amount of introduced filler, able to entrap in its pores vanadium solution, and the amino groups presence able to neutralise the acid sulphonic groups of the polymer, depending on the sulphonation degree.

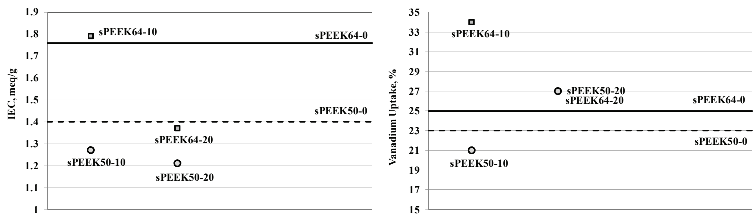

Fig.1a) IEC measurements results 1b) Vup% measurements results

The proton conductivity, vanadium permeability and selectivity data are reported in table 1. The proton conductivity data are in accordance to the vanadium uptake measurements. In fact, membranes with the lowest DS have a lower conductivity than the those having a higher DS, as a function of filler percentage and sulphonation degree.

The permeability measurements are in progress. In any case, the results till now obtained on the composite 64%DS sPEEK membranes reveal an higher permeability value for the membrane with the highest Vup, as expected.

Moreover, the selectivity parameter increases with the filler percentage increase in association with a lower conductivity.

Table 1 Conductivity and permeability/selectivity data for developed membranes

Membrane	Conductivity sigma(S cm^{-1})	Permeability P ($cm^2 \cdot s^{-1}$)	Selectivity phi (10^6 S s cm^{-3})
sPEEK50-0	$1.59 \cdot 10^{-2}$	-	-
sPEEK50-10	$6.12 \cdot 10^{-3}$	-	-
sPEEK50-20	$1.94 \cdot 10^{-2}$	-	-
sPEEK64-0	$2.18 \cdot 10^{-2}$	-	-
sPEEK64-10	$4.9 \cdot 10^{-2}$	$2.60\ 10^{-9}$	18.8
sPEEK64-20	$2.00 \cdot 10^{-2}$	$9.09\ 10^{-10}$	22.4

Conclusions

Two different sulphonation degrees were used to prepare sPEEK membranes for VRBs application. The developed membranes were chemical-physically and electrochemically characterised in terms of IEC, Vup%, vanadium ion permeability and proton conductivity. Consequently the selectivity to vanadium ions was calculated. Considering the obtained results, these membranes seem to be promising for VRBs application, above all regarding the reported selectivity data that are higher than those reported in literature[1] for sPEEK membranes with a similar sulphonation degree.

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