

[Nafion/(WO₃)_x] hybrid membranes for vanadium redox flow batteries

ChuanYu Sun^a, Agnieszka Zlotowicz^a, Graeme Nawn^a, Enrico Negro^{a,b}, Federico Bertasi^a, Gioele Pagot^{a,c}, Ketì Vezzù^a, Giuseppe Pace^d, Massimo Guarnieri^e, Vito Di Noto^{a,b,f,*}

^a Section of Chemistry for Technology, Department of Industrial Engineering, University of Padova, in Department of Chemical Sciences, Via Marzolo 1, I-35131 Padova (PD), Italy

^b Consorzio Interuniversitario Nazionale per la Scienza e la Tecnologia dei Materiali, Italy

^c Centro Studi di Economia e Tecnica dell'Energia "Giorgio Levi Cases", Via Marzolo 9, I-35131 Padova (PD), Italy

^d CNR-ICMATE, Via Marzolo 1, Padova (PD), Italy

^e Department of Industrial Engineering, University of Padova, Via Gradenigo 6/A, I-35131 Padova (PD), Italy

^f Material Science and Engineering Department, Universidad Carlos III de Madrid, Escuela Politécnica Superior, Av.de la Universidad, 30, 28911 Leganes, Spain

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ABSTRACT

Nafion–tungsten oxide hybrid membranes, [Nafion/(WO₃)_x], with varying loading levels of WO₃ nanofiller ($x = 0, 0.024, 0.329$) are prepared and investigated as candidates for application as solid electrolytes in vanadium redox flow batteries (VRFBs). The thermal properties of [Nafion/(WO₃)_x] hybrid membranes are probed both by high-resolution thermogravimetric analysis (HR-TGA) and by modulated differential scanning calorimetry (MDSC). Vibrational spectroscopy studies are carried out by: (i) Attenuated Total Reflectance - Fourier Transform Infrared spectroscopy (ATR-FTIR); and (ii) Raman spectroscopy, to elucidate the secondary structure of [Nafion/(WO₃)_x] and study the interactions taking place between the nanofiller and the Nafion matrix. The electrical response of [Nafion/(WO₃)_x] is determined by Broadband Electrical Spectroscopy (BES) and the permeability towards VO²⁺ is measured by UV-VIS spectrometry. It is demonstrated that the [Nafion/(WO₃)_x] hybrid membranes exhibit a high ion selectivity (up to $10.6 \cdot 10^3 \text{ S} \cdot \text{min} \cdot \text{cm}^{-3}$ for [Nafion/(WO₃)_{0.329}]) that is much improved in comparison with that characterizing recast Nafion ($6.5 \cdot 10^3 \text{ S} \cdot \text{min} \cdot \text{cm}^{-3}$). A structural model and a conductivity mechanism for the [Nafion/(WO₃)_x] hybrid membranes are proposed, in order to rationalize the experimental results and correlate the electrical response with the transport properties.

1. Introduction

In recent years, Vanadium Redox Flow Batteries (VRFBs) have seen a resurgence in research activity owing to their potential as large electrochemical energy storage systems [1–14]. VRFBs benefit from a long cycle life, a high energy efficiency, low cost, and flexible design [15]. VRFBs exploit the different oxidation states of vanadium by using two electrochemical couples ($\text{V}^{2+}/\text{V}^{3+}$ and $\text{V}^{4+}/\text{V}^{5+}$) in an aqueous acidic medium [15–18]. Proton exchange membranes (PEMs) are a key component of numerous electrochemical energy conversion and storage devices and are found at the heart of all VRFBs. The role of PEMs in VRFBs is to provide a barrier against crossover between cathode and anode, and facilitate selective ion transfer during operation [19]. The ideal membrane for application as a separator in VRFBs should not only exhibit a high proton conductivity, but also demonstrate a low permeability towards vanadium species, a good stability and be of low cost. The perfluorosulfonic membranes, Nafion® being the highly renowned, are widely used in VRFBs on account of their high proton

conductivity and high electrochemical stability [15]. However, Nafion membranes suffer from a high vanadium crossover, that causes a long-term decrease in cell efficiency. One way to tackle this issue has been the development of hybrid inorganic–organic membranes based on Nafion doped with inorganic or organic materials. For example, a number of papers report membranes based on Nafion modified with: ZrO₂ [13], TiO₂ [12], SiO₂ [20], organic silica modified TiO₂ [3], metal phosphate hydrate [21], polyaniline [22], polypyrrole [22,23], polyelectrolyte [24], sulfonated poly (ether ether ketone) [2], fluorocarbon [3], amino-silica [10]. According to our previous studies [25–27], the distribution of nanofillers in the polymeric Nafion matrix and the compatibility between the two phases (inorganic filler phase and polymer phase) play an essential role in defining the physicochemical properties of the nanocomposite membranes. Here we describe nanocomposite Nafion-based membranes containing a dispersion of tungsten oxide nanoparticles (NPs) in various weight percentages (*i.e.*, 0, 1, and 12 wt%). These values are selected to better elucidate the impact of the interactions between the WO₃ nanofiller and the Nafion polymer host.

* Corresponding author at: Section of Chemistry for Technology, Department of Industrial Engineering, University of Padova, Via Marzolo 1, I-35131 Padova (PD), Italy.
E-mail address: vito.dinoto@unipd.it (V. Di Noto).

In detail, the membrane including 1 wt% of WO₃ reveals how even a very small amount of nanofiller affects the Nafion matrix. On the other hand, the membrane including 12 wt% of WO₃ highlights the interplay between: (i) the distribution of nanofiller in the membrane, and (ii) the thermal stability, the conformation of the polymer chains and the permeability to vanadium species.

2. Experimental

2.1. Reagents

A 5 wt% solution (water/propanol) of Nafion ionomer (perfluorosulfonic acid PTFE copolymer solution) with an ion-exchange capacity (IEC) of 0.92 meq·g⁻¹ (Alfa Aesar, ACS) is used. The WO₃ nanopowder is used as a homogenous suspension obtained by sonicating WO₃ nanopowders with a particle size of ca. 100 nm (Aldrich, ACS grade) in *N,N*-dimethylformamide (DMF) for 2 h. All the used solvents are provided by Aldrich and used as received; doubly distilled water is used throughout the experiments.

2.2. Membrane preparation

[Nafion/(WO₃)_x] hybrid membranes are prepared with a solvent casting procedure as reported in our previous publication [27]. Briefly, the solvent is removed from the 5 wt% Nafion solution by heating at 80 °C until a thin film is obtained. The film is then dissolved in DMF and mixed with different amounts of WO₃. The resulting suspension is treated in an ultrasonic bath for 2 h, yielding a homogenous dispersion that is cast in a Petri dish (diameter: 90 mm) and placed in an oven at 80 °C for 12 h. The obtained membrane is then dislodged by immersing the Petri dish in bidistilled water at room temperature (25 °C). The thickness of all the membranes in this study falls between 50 and 65 μm (as measured under ambient air conditions).

2.3. Membrane activation

The [Nafion/(WO₃)_x] hybrid membranes are activated in a four-step process. The membranes are heated at 80 °C in bidistilled water for 1 h. They are then removed from the water and immersed in a 3 wt% H₂O₂ solution for an additional hour at 80 °C. The membranes are then soaked for 1 h in 1 M H₂SO₄ at 80 °C, before finally being washed thoroughly with bidistilled water. The treated membranes are stored at room temperature inside plastic bags filled with bidistilled water. Three different membranes are obtained, with *x* = 0, 0.024 and 0.329 (corresponding to 0, 1 and 12 wt%, respectively). The membrane with *x* = 0 does not include WO₃, it is used as the benchmark throughout this work and is labeled “recast Nafion” (Table 1).

2.4. Instruments and methods

High-resolution thermogravimetric analyses (HR-TGA) are executed by means of a TGA 2950 thermobalance (TA Instruments). Approximately 6 mg of sample is loaded onto a platinum pan, with

Table 1
Composition and molar ratios of [Nafion/(WO₃)_x] membranes.

Membrane	Wt% of WO ₃ ^a	<i>x</i> ^b	Ion exchange capacity (φ) ^c /meq·g ⁻¹
Recast Nafion	0	0	0.9200
[Nafion/(WO ₃) _{0.024}]	1	0.024	0.9108
[Nafion/(WO ₃) _{0.329}]	12	0.329	0.8096

^a Values determined on the activated membranes as the high-temperature residue measured on HR-TGA under an air atmosphere.

^b *x* = molWO₃/mol-SO₃H.

^c φ = meq_{Nafion}/m_{composite}.

measurements carried out under a nitrogen or air flux of 100 cm³·min⁻¹ over a temperature range between 20 and 900 °C. The heating ramp is varied from 50 °C·min⁻¹ to 0.001 °C·min⁻¹ on the basis of the first derivative of the weight change. The resolution is 1 μg. The samples are exposed to a dry air flow for 24 h before the measurements (this yields λ ~ 2, where λ is defined as the ratio between the number of water molecules and the number of -SO₃H groups present in the system [28]). Modulated Differential Scanning Calorimetry (MDSC) analyses are carried out using a DSC Q20 machine (TA Instruments) equipped with a liquid nitrogen cooling system. Measurements are executed in modulated mode over a temperature range of -150 ÷ 200 °C with a ± 1.000 °C modulation every 60 s. Approximately 7 mg of sample (desiccated under a dry air flow) is loaded inside a hermetically-sealed aluminum pan. Attenuated total reflectance - Fourier transform infrared spectroscopy (ATR-FTIR) in the medium infrared range is achieved using a Nicolet Nexus spectrometer. FT-IR measurements are collected on both faces of each membrane; the spectra are obtained averaging 1000 scans. Raman spectra are obtained using a DXR-Micro Raman (Thermo Scientific) spectrometer. Samples for ATR-FTIR are prepared in two different conditions: (i) storing samples at room temperature for 24 h under a dry air stream; this yields λ ≈ 2; and (ii) drying the samples at 100 °C under vacuum for 3 days; this yields λ = 0. Condition (i) and (ii) are labeled “air flow condition” and “dry condition”, respectively. The samples for Raman studies are prepared exclusively in “air flow condition”. Broadband Electrical Spectroscopy (BES) is conducted using a Novocontrol Alpha-A Analyzer. A frequency range of 30 MHz ÷ 10 MHz, temperature range of -100 ÷ 200 °C and a 10 °C temperature interval is used for all the samples. The temperature is monitored by using a homemade cryostat operating with a N₂ gas jet heating and cooling system. Circular membrane samples with a diameter of 13 mm are sandwiched between two circular platinum electrodes separated by an optical fiber (d = 0.126 mm) and closed inside a cylindrical cell. BES studies are carried out on completely hydrated samples. The permeability of the membranes is measured by UV-Vis spectrometry using a Lambda Technologies, Lambda 40 UV-Vis dual-beam spectrometer with quartz cuvettes.

2.5. Water uptake, vanadium permeability, ion selectivity and chemical stability

The water uptake (WU%) of the membranes is gauged by comparing the weights of the dry and the wet membrane samples by means of Eq. (1). The dry membrane weight (W_{dry}) is obtained by drying the sample at 100 °C for 12 h immediately before weighing it. The weight of the corresponding membrane in wet conditions (W_{wet}) is obtained by immersing the membrane sample in bidistilled water for 24 h, wiping off the surface moisture with filter paper and then quickly weighing it. The final water uptake is obtained from the average of three experiments.

$$WU\% = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (1)$$

The vanadium permeability is determined using a standard diffusion cell setup [3]. The effective area of the sample membrane is 3 cm². One reservoir is filled with 50 mL of solution consisting of 1 M VOSO₄ in 4 M H₂SO₄; the other reservoir (blank) is filled with a 50 mL solution of 5 M H₂SO₄. The cell is left for 72 h with both halves kept under constant magnetic stirring. 1 mL aliquots are taken from both halves of the cell every few hours over a period of 3 days. The aliquots taken from the blank cell are then tested for vanadium content by means of UV-Vis spectroscopy without diluting the samples. The vanadium permeability (P) of the samples is calculated by means of Eq. (2).

$$V_B \frac{dC_B(t)}{dt} = A \frac{P}{L} (C_V - C_B(t)) \quad (2)$$

where P is the VO²⁺ permeability, C_V and C_B(t) are the VO²⁺ ion concentrations in the vanadium and blank cells, L is the thickness of the

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