

Synthesis and characterization of silicotungstic acid based organic–inorganic nanocomposite membrane

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Abstract

Organic–inorganic composites consisting of silicotungstic acid and poly(vinyl alcohol) were prepared by a sol–gel method. The advantage of this strategy is that it is to manipulate the desired properties such as thermal stability, conductivity. The silicotungstic acid present in the composite acts as acid catalyst to hydrolyze/condense the silica precursor that leads to isotropic composite. The composite is structurally characterized with various techniques such as IR, UV–vis, TGA, SEM, TEM and CV measurements. The proton conductivity of composites is measured using impedance spectroscopy. The conductivity is found to increase with increase in temperature. The activation energy for the proton migration in the composite film was calculated to be 10 kJ/mol.

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1. Introduction

Fuel cells are extremely attractive energy conversion devices for transportation and portable applications due to their high efficiency and low emission [1]. Among several types of fuel cells, polymer electrolyte membrane fuel cells (PEMFC, DMFC) have been regarded as promising options for electrical vehicles. The vital component in PEMFC is proton conducting membrane. The necessary criteria of the membrane for the PEMFC applications are (i) high specific conductivity (0.1 S/cm^2), (ii) good water retention, (iii) durability and (iv) low cost. Among the available membranes (Dupont, Dow, Aciplex®, Gore and Asahi) Dupont's Nafion® is the most advanced commercially available proton conducting membrane, which is produced in membrane form with thickness ranging from 25 to 175 μm . This material shows excellent proton conducting property and high durability in fuel cell environments. However, it has severe limitations, which restricts the extensive use in fuel cells. The Nafion® membrane functions as proton conductors only in a highly hydrated state, so humidification is necessary [2]. The main limitation with Nafion® is that it has poor methanol barrier (high crossover), so

significant quantities of methanol diffuse through the membrane, and hence it reduces the efficiency at cathode (mixed potential) and develops methanol concentration gradient at anode. Also its high water permeability (swelling) reduces the efficiency at the cathode [3].

There is a strong driving force to operate PEMFCs at higher temperatures. In DMFC, the increase to high temperatures ($130\text{--}200^\circ\text{C}$) improves the kinetics of the methanol oxidation reaction at the anode, which will enhance the efficiency of the cell significantly. In $\text{H}_2\text{--O}_2$ fuel cell, the high temperatures (150°C) will allow the fuel cell to tolerate higher levels of carbon monoxide [4] (produced as a by product in the fuel reformer). When the synthesis of perfluorinated sulfonic acid (Nafion) is considered, fluorination of backbone is synthetically challenging and as well as the processability of membrane is difficult.

The most logical approach to develop a high temperature proton membrane would be to adopt materials, which do not require water to maintain their proton conductivity. Considering these facts, the drop of conductivity at elevated working temperatures, two strategies have been developed. The first one relies on polymer systems with high resistance to dehydration or those capable of maintaining a high conductivity with low levels of water content. The other system concerns anhydrous system where the migration of proton is not assisted by water. Moreover in the former system, the synthesis of polymer is difficult and to

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get the conductivity there should be a functional group on the backbone.

The alternatives can be organic–inorganic hybrids, they are a remarkable family of isotropic, flexible, amorphous materials [5]. Besides the blending properties of the hybrids, they can also be easily synthesized through processing routes with low cost and lesser environmental impact. The physicochemical properties (thermal stability, conductivity, mechanical stability) can be altered at molecular levels by adjusting the individual components.

It is appropriate that some comments on the general aspects of these membranes are considered. It is always perceived that such composite membranes might contribute to the energy loss, but however, these membranes have been shown to exhibit good conductivity of the order of 1×10^{-2} S/cm at 393 K [6]. The organic polymers give the flexibility to the composite, the inorganic component present in the composite enhances the stability (thermal, mechanical, hydrolytic) and the active component (polyoxometalates—conductivity 0.17 S/cm) gives the value adding property to the hybrid composite. Heteropolyacids doped in polymers have been employed as proton conducting gels [7]. Organic/inorganic nanohybrids have been prepared based on heteropoly compounds [8–11].

The protonic conductivity of these membranes is unique feature, since both the inorganic component, silica and other oxides as well as the active component (heteropolyacids) are capable of sustaining a large number of water molecules in their hydration sphere, so that the proton migration can be as effective as in aqueous electrolyte solutions. The functionalities that can be generated in the inorganic component of the membrane, can be effectively utilized for anchoring the active component and by this way the decay of the membrane performance can be considerably reduced as well as the identity of the active component in nano segregated scale can be retained which will facilitate the protonic conductivity. Another aspect of these membranes is that the aqueous solubility of the active component, namely the heteropolyacids could be effectively reduced, by ion exchange of the protons with large cations like Cs^+ , Rb^+ , TI^+ . This could considerably reduce the effective conductivity of the membrane, but still the conductivity of these membranes is of the order of 1.2×10^{-2} S/cm at 393 K. It is necessary at this stage to reflect on the possible utility of these composite membranes in comparison to the conventional Nafion membrane. Ramani et al. have prepared these types of membranes, wherein the active component was embedded in Nafion in the presence of the higher boiling solvent the DMF as well as using Na^+ exchanged Nafion [12]. They have shown that these membranes can be employed for high temperature (393 K) operations at low relative humidities. The conductivity values of these membranes are of the order of 1.5×10^{-2} S/cm. The conduction mechanism in these composite membranes can be a combination of vehicular and Grotthuss mechanism, and conductivity and fabrication procedures could be suitably tailored to have one or the other forms of conduction predominates in the membranes generated. Since a variety of heteropoly acids based on either P or Si, or on W or Mo, together with their insoluble salts can be utilized, membranes with tailor made properties appear to be a feasible proposition.

The aim of this work has been the synthesis and characterization of organic–inorganic nanocomposite membrane based on silicotungstic acid. The composite membranes have been synthesized by sol–gel method. The synthesized composite membranes were characterized with IR, UV–vis, TGA, SEM, TEM, CV and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Materials

Silicotungstic acid (SiW) and polyvinylalcohol (72,000) were purchased from SRL chemicals and tetraethyl orthosilicate was purchased from the E-Merck. All other chemicals were reagent grade and were used as received. Glassy carbon electrode (3 mm) was procured from Bioanalytical Systems (BAS), USA.

2.2. Synthesis of composite

The organic–inorganic composite was prepared by sol–gel method [13]. A solution of polyvinyl alcohol (PVA) in water in the range of 30 wt% adding to the selected solution 20 wt% tetraethyl orthosilicate and the silicotungstic acid (50 wt%) was added and then refluxed the resultant at a temperature 353 K for 6 h, to obtain a clear viscous gel. The final transparent solution was used to make films for further studies. The silicotungstic acid ($\text{H}_4\text{SiW}_{12}\text{O}_{40}$) acts as acid catalyst for hydrolysis and promotes the condensation of the tetraethyl orthosilicate present in the precursor. The crosslinking between the silica matrix and polyvinyl alcohol takes place in presence of POM. The polyoxometalate is entrapped in the polymer matrix by interacting with the hydroxyl groups of polymer. The transparent gel was made into films by drop casting method. The thickness of the membrane films were varied from 60 to 100 μm .

2.3. Apparatus

Transmission electron microscopic (TEM) images were taken using Philips CM12/STEM, Scientific and Analytical Equipment. TEM sampling grids were prepared by placing 2 μl of the solution on a carbon-coated grid and the solution was evaporated at room temperature. Electrochemical measurements were performed on a BAS Epsilon potentiostat for cyclic voltammetric studies and PARSTAT 2263 electrochemical analyzer for impedance measurements. Cyclic voltammograms were recorded on a three-electrode assembly with modified glassy carbon as working electrode, Ag/AgCl (saturated KCl) as reference electrode and a platinum foil (1.5 cm^2) as auxiliary electrode. All potentials were measured and reported with reference to Ag/AgCl electrode. One molar sulphuric acid was employed as supporting electrolyte. Electrochemical impedance measurements were carried out by using standard three-electrode system, recorded in the frequency range of 100 kHz–100 mHz by using a sinusoidal excitation signal (single sine) with an excitation amplitude of 5 mV. The impedance data were analyzed using ZsimpWin EIS DATA analysis software (Perkin-Elmer, Version 3.10) by fitting into an appropriate equivalent circuit.

2.4. Fabrication of electrode

The glassy carbon was first polished with alumina paste (procured from BAS) followed by ultrasonication in water for 5 min and then polished with diamond paste (3 μm) further ultrasonicated for 10 min in water. The composite was coated on glassy carbon electrode by taking 10 μl of PVA–SiO₂–SiW composite and dried in oven at 80 °C for 2 min to get a thin film on GC electrode (PVA–SiO₂–SiW/GC). This was employed as working electrode for the further studies.

3. Results and discussion

Fig. 1 shows the infrared spectra of PVA–SiO₂–SiW film. The positions of vibration modes of all types of M–O bonds are strongly affected by the interactions with the polymer. Therefore, the spectra of parent SiW and composite film have been compared. It is found that the frequencies of SiW in the composite film are blue shifted. A detailed inspection of the band of W=O_t bond of SiW in the composite is red shifted from 964 to 954.7 cm^{-1} , and the band of W–O_c–W from 868 to 855 cm^{-1} . The band of W–O_b–W has a blue shift from 776.1 to 799.9 cm^{-1} . This may be due to the columbic interaction between the hydroxyl groups of the polyvinyl alcohol donor and the silicotungstic acid. IR absorption peaks at 1066 cm^{-1} (Si–O–C) and (Si–O–Si), 1662 and 796 cm^{-1} indicate the development of an organic–inorganic hybrid network during the gel formation. In addition there are several strong bands below 1100 cm^{-1} due to polyoxometalates. It is found that the frequencies of SiW in the hybrid film are shifted from those of pure SiW by only a few cm^{-1} , which indicates that the Keggin geometry of SiW is still preserved inside the gel. A more detailed inspection of the vibrational band shift reveal that vibrational bands of the W=O_t bond of SiW in the composite film is red shifted from 983 to 980 cm^{-1} and the band Si–O, from 1086 to 1076 cm^{-1} . The bands of W–O_b–W and W–O_c–W both have blue shifts from 891 and 803 cm^{-1} to 897 and 809 cm^{-1} , respectively, due to the presence of coulombic interactions between the donor (organic composite) and acceptor (HPA) species.

Oxygen to metal charge transfer band observed at 265 nm for the parent SiW and for the composite film band is shifted to higher wavelength. This shows that the polyoxometalate is interacting with the polymer hydroxyl groups. The composite gel

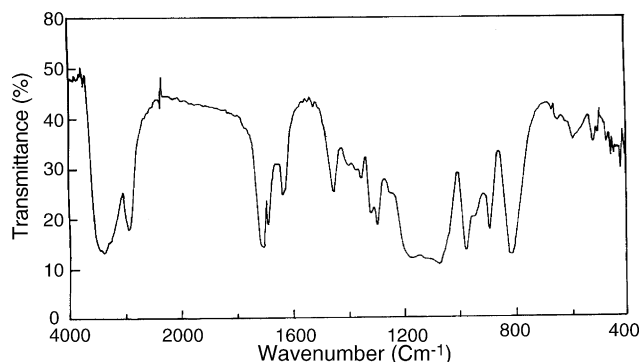


Fig. 1. Infrared spectra of organic–inorganic composite PVA–SiO₂–SiW.

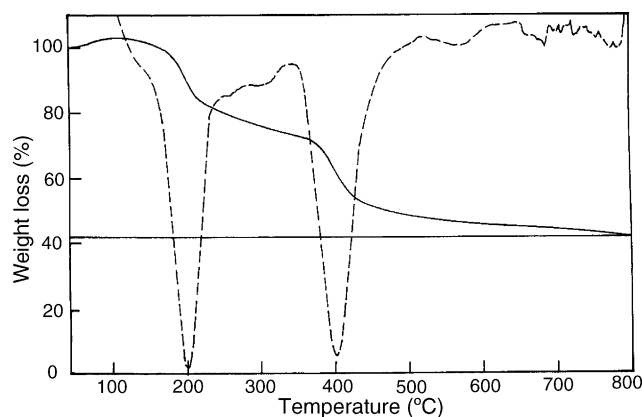


Fig. 2. TG-DTA analysis of the PVA–SiO₂–SiW in a temperature range from 50 to 800 °C.

was coated on quartz plate and UV–vis spectra were recorded. A band at 298.8 nm was observed. A characteristic oxygen to metal charge transfer band observed at 265 nm for parent polyoxometalates. This band was red shifted in composites, which shows that the polyoxometalate is interacting with the polymer hydroxy groups as well as with the silica. This was further supported by infrared spectroscopy and cyclic voltammetric studies.

Fig. 2 illustrates the thermogravimetric analysis of composite film. Initial weight loss is due to water in the temperature region 60–100 °C and a major second weight loss is due to decomposition of polyvinyl alcohol in the temperature region 200–300 °C. The third weight loss is due to decomposition of silicotungstic acid to respective metal oxides.

The surface of the composite was examined with scanning electron microscopy. It is evident from the images that the organic–inorganic composite structure is highly homogeneous in nature. The dispersed silicotungstic acid can be seen from the high resolution SEM image (Fig. 3). The microstructure of composite film can be visualized through the transmission electron microscopy. The embedded particles are spherical in shape and having the size of 10–20 nm is evidenced from Fig. 4. Thus, one could effectively disperse the active components in controlled manner through organic–inorganic synthetic strategies.

Fig. 5 illustrates the cyclic voltammograms of composite film coated on GC. The cyclic voltammogram of PVA–SiO₂–SiW showed four anodic peaks (E_{pa} at –231, –426, –592 and –716 mV) and four cathodic peaks (E_{pc} at –264, –487, –646, –915 mV). One electron formal potential for silicotungstic acid in 1.0 M sulphuric acid was observed at –228 mV [14]. The peak potentials shifted towards more negative when silicotungstic acid was present in composite environment when compared to the parent compound [15]. This might be due to the stabilization of energy levels of polyoxometalate upon embedding. The cyclic voltammograms were carried out in the potential window of –1000 to 200 mV for 500 cycles. There was no appreciable decrease in the cathodic or anodic current upon cycling which reveals the firm entrapment of polyoxometalate in the composite. EIS is an effective method to study the interfacial properties of modified electrodes [16–18]. It is extensively used to understand the charge transfer phenomenon in polymer-modified

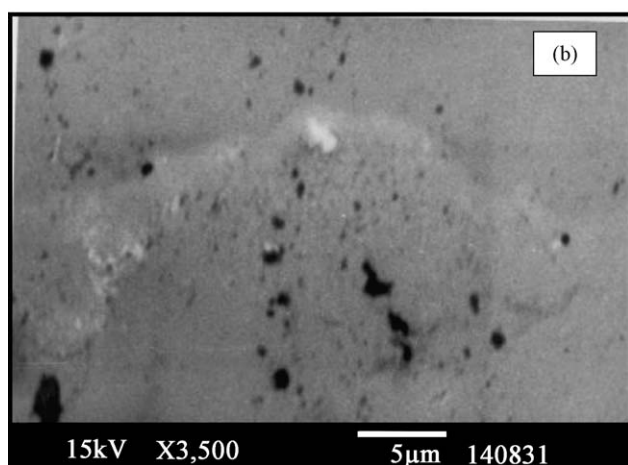
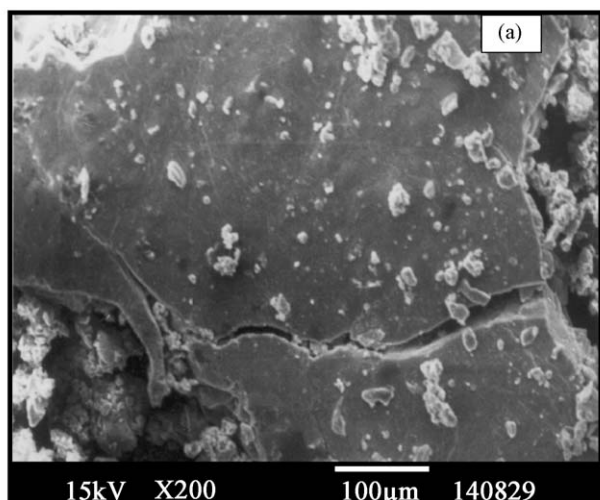


Fig. 3. Scanning electron micrographs of PVA-SiO₂-SiW: (a) low magnification and (b) high magnification.

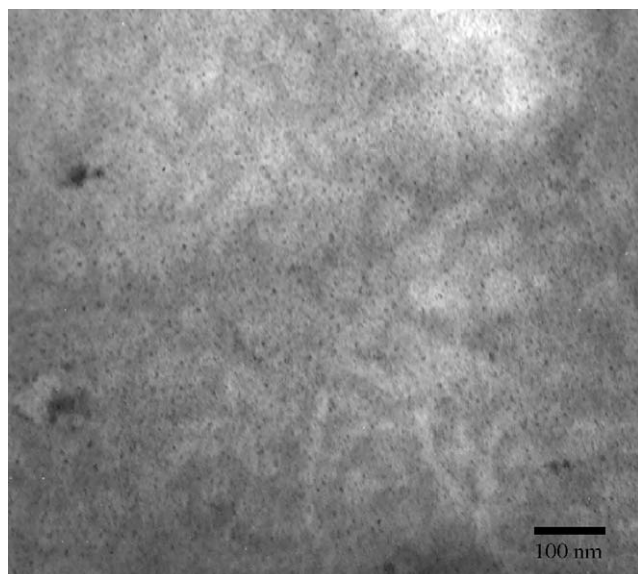


Fig. 4. Transmission electron micrograph of PVA-SiO₂-SiW.

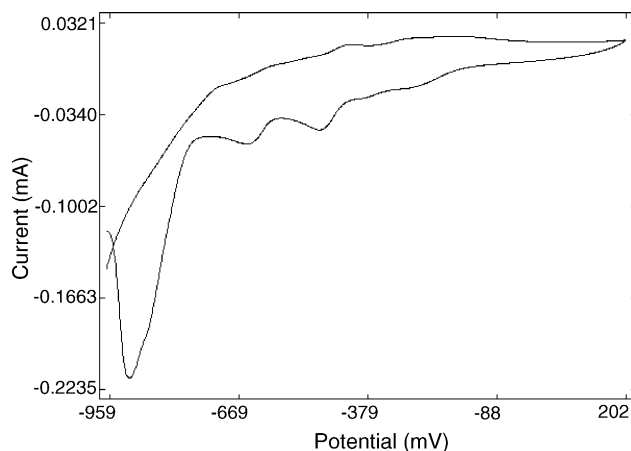


Fig. 5. Cyclic voltammogram of PVA-SiO₂-SiW on GC at 25 °C in 1 M H₂SO₄, scan rate 25 mV S⁻¹.

electrodes. Dependence of potential and pH of the electrolyte can be evaluated from the EIS study and it alters some features of the impedance data on the electrode surface, e.g., the double layer capacitance, charge transfer resistance and Ohmic resistance. The complex impedance can be represented as a sum of real and imaginary impedance components, which are mainly contributed from the resistance and capacitance of the cell. The complex plot Z_{re} versus Z_{im} shows a semicircle at high frequency region and a straight line having slope of 45 at low frequency region, which is a characteristic plot for polymer-modified electrode. The Ohmic and charge transfer resistance were extracted from the complex plot.

Nyquist plot of composite coated on GC in 1.0 M sulfuric acid shows a depressed semicircle at high frequency region and a spike boost at low frequency region. The high frequency impedance is contributed from the charge transfer resistance along with the Ohmic resistance and the low frequency impedance is due to the diffusion of the electron from the active species present in the composite. All the experimental data were interpolated using the equivalent circuit, which was able to fit all the spectra, giving χ^2 values of the order of 10^{-4} to 10^{-3} .

The impedance measurements were carried out at different temperatures and the values of charge transfer resistance and double layer capacitance were extracted from the Nyquist plots by fitting into their equivalents circuit. Temperature dependence of the conductivity for PVA-SiO₂-SiW is shown in Fig. 6, which is of Arrhenius type. The presence of silica in the composite membrane and the 100% relative humidity allow the membranes to maintain almost stable proton conductivity. Conductivity measurements performed at higher temperatures, in the range from 80 to 100 °C, give almost stable values of $(4.13\text{--}8.31) \times 10^{-3}$ S/cm. The proton migration is dominantly through the Grotthuss mechanism. In this mechanism, the proton forms hydrogen bond with the water molecules and exits as H₃O⁺ and hopping from one active component to other through tunneling mechanism. The activation energy for the proton migration was calculated and found to be 10 kJ/mol, which is in the range of activation energy for Grotthuss mechanism.

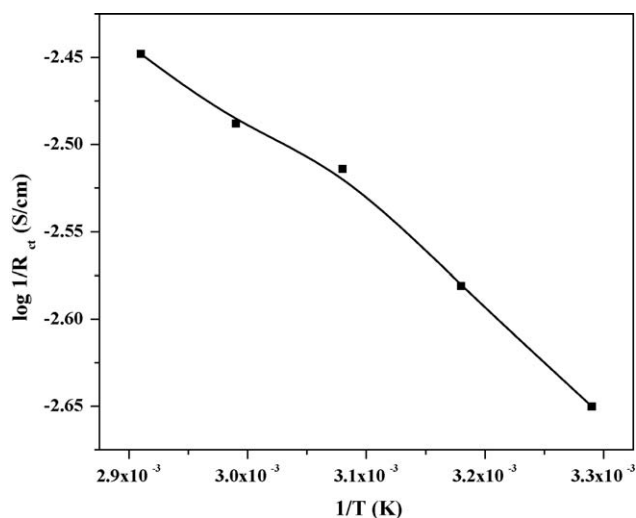


Fig. 6. Conductivity as a function of inverse temperature for PVA–SiO₂–SiW.

4. Conclusion

The organic–inorganic composite was synthesized through the sol–gel method. The composite membrane films have been characterized with various physico-chemical techniques. The composite doped with silicotungstic acid exhibits high conductivity in the temperature range 30–100 °C. The composite was found to be thermally stable at high temperature because of the inorganic silica framework in the matrix. Conductivity measurements performed at higher temperatures, in the range from 80 to 100 °C, give almost stable values of $(4.13\text{--}8.31) \times 10^{-3}$ S/cm at 100% relative humidity. The conductivity and thermal stability of the composite membrane can be fine tuned by altering the individual components at the molecular levels.

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