 DOI: 10.1002/masy.201051014

Synthesis and Characterization of Novel Sulfonated Hybrid Congo Red Membranes from Chlorofunctionalized Silsesquioxanes for Fuel Cell Application

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A new sulfonated copolymers containing congo red groups were synthesized as a potential electrolyte for high temperature PEFCs. The resulting cross-linked sulfonated hybrid congo red membranes showed greatly improved water stability in comparison with the uncrosslinked ones while high proton conductivity was maintained. sulfonated membranes have been tested with respect to fuel cell performance. Short term fuel cell test for 100 hr gave a stable performance. These membranes are less expensive compared to Nafion. New sulfonated proton exchange composites membranes were used biological fuel cells. Molasses which is the waste of sugar factory, was used in anode as fuel and different bacteria species was sowing. Potential change was reported in biological fuel cells.

Keywords: congo-red; microbial fuel cell; PEM membrane; POSS

Introduction

Fuel cells are attractive alternatives to combustion engines as electrical power sources because of their high efficiencies and low pollution levels.[1] Polymer electrolyte membrane (PEM) is the key component of a fuel cell system.[2] Current state-of-the-art PEMs used in practical systems are sulfonated perfluoropolymers, typically DuPont's Nafion, which have high proton conductivity, good mechanical properties, and high thermal, chemical and electrochemical stability. Since protons migrate as hydronium ions, it is crucial to retain water molecules within hydrophilic domains of membranes. At elevated temperatures above 100 °C, perfluorosulfonic acid polymer suffers from lowered conductivity due to the loss of water. Lack of interaction (or cross-linking) among polymer chains gives rise to insufficient mechanical strength.[3–6] There has been extensive research work to develop alternative proton conductive polymer electrolyte membranes.

Microbial fuel cells (MFCs) are devices that use bacteria as the catalysts to oxidize organic and inorganic matter and generate current.[7–11] In MFC, microorganisms oxidize organic matter in the anode chamber producing electrons and protons. Electrons transfer via an external circuit to the cathode chamber where electrons, oxygen and protons combine to produce water. Electrons can be transferred to the anode by electron mediators or shuttles,[12,13] by direct membrane associated electron transfer,[14] or by so-called nanowires[15] produced by the bacteria, or perhaps by other as yet undiscovered means. During electron production protons are also produced in excess. These protons migrate through the proton exchange membrane (PEM) into the cathode chamber.[16] Chemical mediators, such as potassium ferricyanide, can be added to the system to allow electricity production by bacteria unable.

The present investigation focuses on the preparation of hybrid Congo Red with the

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development of polyhedral oligomeric silsesquioxane (POSS) framework by the sol-gel process in which the symmetrical structure of Congo Red and its charge separation were prevented by introducing the silica cage (POSS) by forming a novel hybrid Congo Red pigment. Congo Red dye has been bonded to the functionalized octameric polyhedral silsesquioxanes (POSS) which was prepared by hydrolytic condensation of chloro functionalized organosilicon monomers in the presence of a catalyst. The binding reaction of Congo Red to the POSS with chloro groups was achieved the addition of the Congo Red via HCl elimination. Prepared novel sulfonated hybrid congo red membranes were tried for fuel cell application.

In this work, we try partially to fill this gap by giving a method of preparation of the POSS molecules from γ-chloropropyltrimethoxy silane (CLS) by the sol-gel process in the presence of a catalyst. In this work our objective is four fold: (1) to give the experimental conditions to prepare the POSS molecules, (2) to elucidate the structure by means of X-ray diffraction (XRD) studies, Fourier transform infrared spectroscopy (FT-IR), and ^{13}C- and ^{1}H nuclear magnetic resonance (NMR) spectroscopy. (3) to prepare nano particular Congo Red POSS molecules from CLS. The last aim (4) is fuel cell application of the prepared novel sulfonated hybrid congo red membranes. The sulfonated membranes have been characterized for their ion Exchange capacity (IEC), thermal properties and ionic conductivity. This membranes have been tested for unit cell performance in microbial fuel cell.

Experimental Part

Materials and Methods

All reactions were performed under an atmosphere of dry nitrogen using standard Schlenk techniques Solvents and chemicals were obtained from Aldrich and used as received unless specified otherwise. Congo red (CR) was used as received since the dye content was verified as to be 97%. An ultrapure water filtering system was used to produce deionized water, and methanol was dried over calcium hydride.

Infrared spectra were recorded as KBr pellets in the range 4000–400 cm^{-1} on an ATI UNICAM systems 2000 Fourier transform spectrometer. ^{1}H NMR spectra (300 MHz) and ^{13}C NMR spectra (75.5 MHz) on a Bruker AM 300 WB FT spectrometer with δ referenced to residual solvent $CDCl_3$. Differential scanning calorimetry (DSC), differential thermal analysis (DTA) and thermogravimetry (TG) were performed with Shimadzu, DTA-50 and TGA-50 thermal analyzers respectively.

Gel permation chromatography (GPC) analyses were performed at 30 °C using N-methyl-2-pyyrolidone (NMP) as eluant at a flow rate of 0.5 mL/min. A differential refractometer was used as a detector. The instrument (Agilent 1100 series GPC-SEC system) was calibrated with a mixture of polystyrene standards (polysciences; molecular masses between 200-1200000 Da) using GPC software for the determination of the average molecular masses and the polydispersity of the samples.

Preparation of Octa-γ-chloropropyloctasilsesquioxane (POSS-CLS)

In each sol-gel polymerization, the monomer solutions and the monomer and catalyst solutions (200 ppm by weight) were sealed in polypropylene bottles, the product was washed with H_2O (3×100 ml) and ether (2×50 ml) and dried under vacuum for 24 h at 100 °C.

A solution of 3-chloropropyltrimethoxysilane (CLS) 45 ml was added in a solution of dry methanol. To this mixture was added 28 ml concentrated HCl, and the reaction mixture was kept at room temperature for 2 days. $PtCl_4$ was added to this solution as catalyst in an argon atmosphere. The reaction mixture was transferred to the Shlenck and heated to 50 °C. A crystalline precipitate formed after a day at 50 °C, was collected and treated as described above. The product has a melting point of 207v°C. And the chlorine content was

found to be 27.6%. The GPC chromatogram indicated monodisperse compound. The product obtained in 45% yield was filtered, and washed with cold methanol and dried in vacuum oven at 30 °C.

Procedure for Binding of Congo Red to POSS-CLS

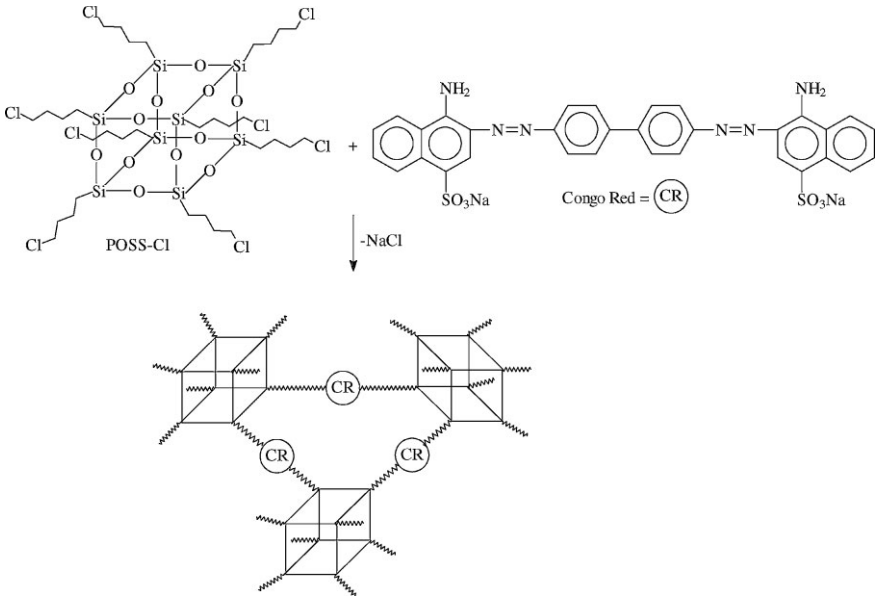
Congo-red (Aldrich, 0.624 g, 0.9 mmol) and POSS-CLS (14.8, 14.34 mmol) are reacted 48 h in refluxing DMSO (25 mL). The solid particles were collected by filtration and extracted with methanol and dichloromethane in a soxhlet apparatus for 24 h to remove unreacted dye molecules that is physically adsorbed. The samples were then dried in vacuum at 110 °C for 2 h.

Determination of Sulfonic Acid Concentration

The sulfonic acid concentration, i.e. sulfonation level or ion exchange capacity (IEC) of each sulfonated proton exchange composites membrane was determined by element analysis (EA). IEC of ion exchange polymers were usually determined by titration,[17–19] but IEC measurement for sulfonated proton exchange composites membranes through titration method using strong base, 0.1N NaOH might cause to decompose sulfonated proton exchange composites membranes. Thus, from the weight of detected sulfur and carbon, the sulfonation levels were quantitatively evaluated by EA.

Fuel Cell Tests

Two-rectangular chambered MFCs (400 mL working volume; 25 mL headspace volume each) were constructed with a separation of sulfonated hybrid congo red proton exchange membrane, a 5 mm electrode spacing, and an external resistance of 100 Ω. The anode consisted of a carbon felt electrode (25 cm^2). The cathode was made from 0,2 M a phosphate buffer with the same size as the anode, with 0,020 M potassium ferricyanide. The anode chamber was inoculated using aerobic biologcal fuel from the waste of sugar factory, and was filled with an autoclaved anaerobic nutrient mineral buffer (pH 7.0) solution, whereas the cathode chamber contained a phosphate buffer (pH 7.0) with continuous aeration. As substrat, glucose from the waste of sugar factory were used. Two



Scheme 1.
Synthetic route fort the preparation of POSS-CLS-CR hybrid dye.

MFCs with different bacteria (*Saccaromyces cerevisia* and *Enterobacter aerogenasa*) were operated with a gentle stirring in a temperature controlled room at 37 °C. Potential change was reported in biological fuel cells. The current voltage characteristics were recorded. The system was operated at ambient pressure.

Results and Discussion

Membrane Characterization

Octafunctional octahedral silsesquioxanes $[RSiO_{1.5}]_8$ (POSS) or cubic silsesquioxanes $[RSiMe_2OSiO_{1.5}]_8$ (cubes) represents three-dimensional nanobuilding blocks. Polyhedral oligomeric silasesquioxanes $(RSiO_{1.5})_{2n}$ ($n = 2, 3, 4$) have attracted considerable interest in the last few years. They are accessible by hydrolysis of trifunctional $RSiY_3$ molecules and can be modified by a number of substitution reactions.[20–21] Thus, functionalized silasesquioxanes have become available, which are interesting as precursors to organolithic macromolecular materials or hybrid inorganic–organic materials. They have become prevalent during the past decade for use in preparing organic-inorganic hybrid materials with precise control tailoring of the nanoarchitecture and properties can be tailored. Congo Red dye has been tailored to the prepared POSS frame work as shown in Scheme 1.

The FT-IR spectra of both frameworks are shown in Figure 1 The tentative assignments for the spectra of the frame work were as follows: 1174 cm^{-1} (asymmetrical) ν_{as} (Si-O-Si), 1060 cm^{-1} ν (Si-O-), 938 and 785 cm^{-1} (symmetrical)ν_s(Si-O-Si), 620 and 550 $cm^{-1}\nu_s$ (Si-O-Si). Polysiloxanes made up tetrahedral (T) units, $[RSiO_{1.5}]_x$,

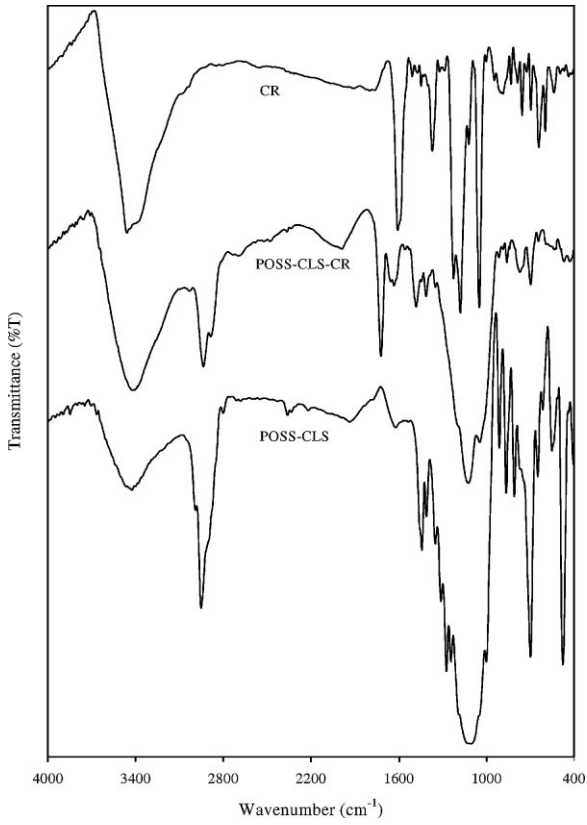


Figure 1.
FT-IR spectra of Congo Red (CR), POSS-CLS and the hybrid pigment (POSS-CLS- CR).

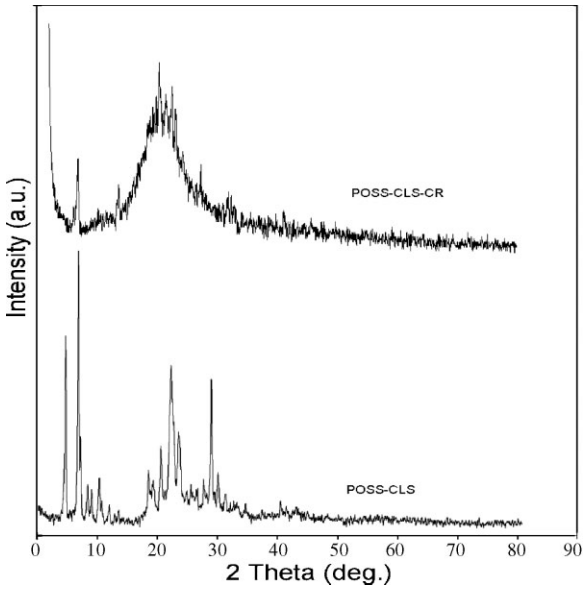


Figure 2.
The XRD patterns of the POSS-CLS the hybrid pigment (POSS-CLS-CR).

showed a broad, structure less absorption covering the entire region of 1160 – 1000 cm^{-1}. The bands observed at 1630, 1280 and 1155 cm^{-1} indicated aromatic C=C vibration, symmetric stretching of S=O, and asymmetric stretching of S=O. However FT-IR spectra of hybrid dye indicated the formation of linkage between $SO_3^-Na^+$ groups and amino groups on CR molecule.

The XRD patterns POSS-CLS are shown in Figures. 2 respectively. The complete lists of observed and calculated interplanar spacing, for both frame works are given in Table 1. The observed pattern for POSS-CLS can be fitted to a hexagonal unit cell with the parameters $a = b = 16{,}77$ Å and $c = 17{,}46$Å.

Figure 3 shows the ultraviolet absorption spectra of Congo Red (CR), POSS-CLS and the hybrid dye POSS-CLS-CR in ethylene glycol. The maximum at 532 nm in the spectra of Congo Red in the hybrid diminished. This fact suggests the formation of complex between POSS frame and Congo Red molecules.

We investigated the morphologies of the Congo Red-POSS hybrid pigment by SEM. Figure (a)–(b) display the SEM cross sectional images of the POSS-CLS (a) and the hybrid pigment (POSS-CLS-CR) (b). In Figure 4(a), the SEM image of the POSS-CLS indicates that the POSS moieties are still dispersed evenly. The POSS-CLS has a dense morphology and crystalline structure. For the POSS-CLS, the light gray spots of about 15–25 nm in size distributed across the dark background are probably the crystalline aggregates of the POSS groups. The voids (dark spots) of about 15–20 nm in size in Figure 4(a) are probably associated with the external porosity, arising from the

Table 1.
Observed and calculated 2θ values using a hexagonal cell with $a = b = 16{,}77$ Å, $c = 17{,}46$ Å and the measured diffraction intensity from the X-ray powder diffraction pattern obtaind from POSS-CLS.

2θ obs./degrees	2θ calc./degrees	*Error (%)*	hkl
10.12	10.12	0	002
11.82	11.82	0	012
18.54	18.54	0	123
19.08	19.08	0	132
22.64	22.72	8	141
27.23	27.20	3	251
28.08	28.08	0	151

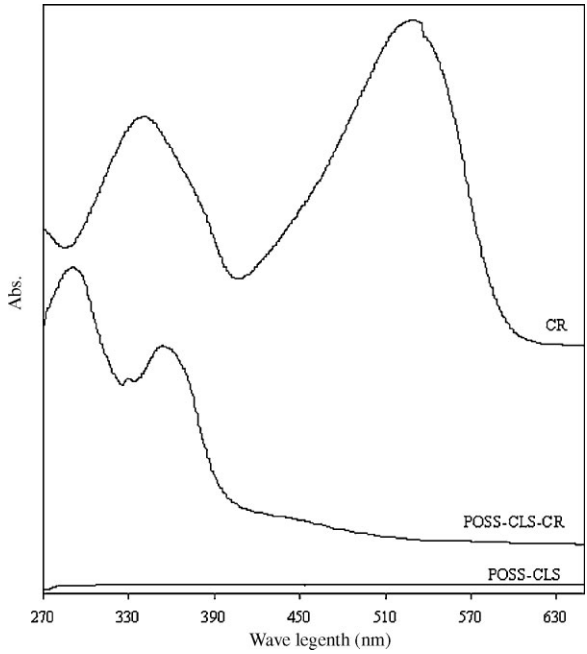


Figure 3.
UV spectra of Congo Red (CR), POSS-CLS and the hybrid pigment (POSS-CLS-CR) in ethylene glycol at room temperature.

stacking of the POSS. In scanning electron micrograph images of the hybrid pigment (POSS-CLS-CR) (4(b)), POSS particles are homogeneously distributed in the hybrid network regularly. Congo Red-POSS hybrid pigment are self-assembled system, so that nanocomposites formed by covalent bonding can be distributed in hybrid network in a way of effectively controlling polyhedral oligomeric silsesquioxane. The POSS groups in hybrid network are well distributed and do not aggregate. It is proposed that the nanostructuring of the Congo Red molecular network is the result of incorporating POSS into the network as illustrated schematically in Scheme 1.

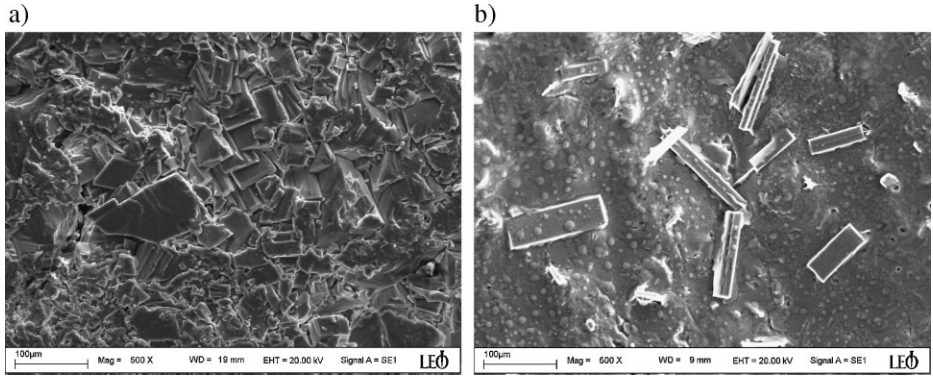


Figure 4.
Scanning electron micrograph images of POSS-CLS (a) and the hybrid pigment (POSS-CLS-CR) (b).

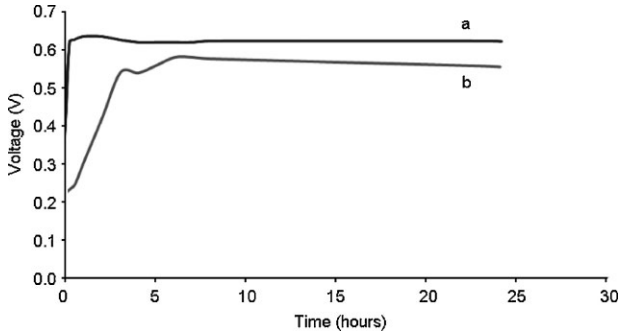


Figure 5.
Course of voltage during short-term testing of sulfonated proton exchange composites membranes in constant current (1 A) mode. ((a) *Saccaromyces cerevisia*, and (b) *Enterobacter aerogenasa*)

Determination of Sulfonic Acid Concentration

The sulfonation level defined as $\varphi = (x/(x+y)) \times 100$ (mol%), where x, y are the sulfonated Congo red and POSS, respectively as shown in Fig. 1. The actual sulfonation level as a function of designed sulfonation level is 15,2 (mol%) and ion exchange capacity is 0,56 mmol/g. Thus, the membrane with the targeted sulfonation level was easily achieved by adjusting the molar ratio of monomers.[22]

Fuel Cell Performance

The *performance* of the membranes in Fuel cell was characterized in the permeation device and desciribed 2.5. Course of voltage during short-term testing of sulfonated proton exchange composites membranes in constant current (1 A) mode are shown Figure 5. The cell was run for 24 hr each bacteria at 37 °C in constant current (1 A) mode without any marked loss in performance.

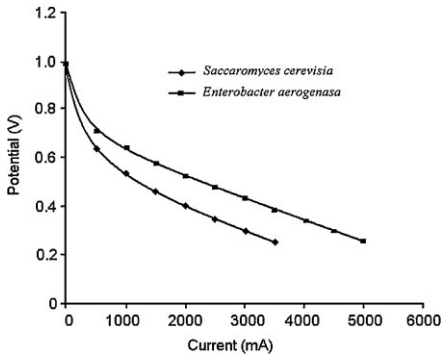


Figure 6.
Polarization characteristics of sulfonated Congo red and POSS with different bacteria (*Saccaromyces cerevisia*, and *Enterobacter aerogenasa*)

Polarization curve of various sulfonated Congo red and POSS membranes are presented in Fig. 6. In literature, it has been observed that acrylic acid grafted PFA membrane had a very poor open circuit voltage of 0.190V (cf. Nafion 117 MEA OCV _0.9 V) and was unable to sustain any current flow.[23] The reason for this poor performance was attributed to the weakly acidic characteristic of –COOH group. Hence in the proton rich environment of the fuel cell, the carboxylic acid group does not dissociate and there is no mechanism for proton conduction resulting in almost nil current flow. A similar trend is expected for sulfonated Congo red and POSS. However, on sulfonation as can be seen from Fig. 6, all the membranes show OCV closer to Nafion 117 and in some cases slightly higher value. This is mainly due to strongly acidic characteristics of $–SO_3H$ group which facilitates proton conduction resulting in good current flow. From Fig. 6, it can be seen that the polarization is better. The cell was run for ~100 hr in constant current (1 A) mode without any marked loss in performance.

Conclusion

In conclusion, a new sulfonated copolymers containing congo red groups was synthe-

sized as a potential electrolyte for high temperature PEFCs. The resulting cross-linked sulfonated hybrid congo red membranes showed greatly improved water stability in comparison with the uncross-linked ones while high proton conductivity was maintained. Sulfonated Congo red-POSS membrane is quite tough and easy to handle. Short-term fuel cell test of these membranes up to 24 hr has given a stable performance.

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