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Multi-Walled Carbon Nanotube/Polyacrylamide Composite Hydrogels as Solid Electrolytes for Microbial Fuel Cells

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ABSTRACT

Microbial fuel cells provide an economically and practically viable option for green generation of electric power from organic pollutants present in waste water with the help of micro-organisms. Several attempts are being made to commercialize the system for stable power generation. For portable applications, the size of the fuel cell and its volumetric power density are major determinants. In this context, microbial fuel cells with a solid electrolyte sandwiched between a cathode and anode would be an attractive configuration. In this work, we report the synthesis and characterization of highly cross-linked multi-walled carbon nanotube/polyacrylamide composite hydrogels as solid electrolyte for application in such devices. The composite hydrogels were synthesized by *in situ* free radical polymerization of acrylamide in presence of surfactant-dispersed multi-walled carbon nanotubes. Ionic conductivity was introduced to the hydrogels by partial hydrolysis in alkaline medium and the conductivity was compared using Electrochemical Impedance Spectroscopy. The composite hydrogels with different loadings of carbon nanotubes were characterized systematically by Differential Scanning Calorimetry, Scanning Electron Microscopy and Swelling studies.

Key words: Fuel cell, carbon nanotube, composite, hydrogel, electrolyte

INTRODUCTION

Microbial Fuel Cell is an energy conversion device that converts microbial activity on organic pollutants present in wastewater into useful electricity. Despite their simpler construction and availability of fuel in abundance, which is nothing but waste water, microbial fuel cells have not been as commercially successful as chemical fuel cells. Poor performance in terms of power output delivered from microbial fuel cell is one of the major factors limiting their practical application (Kim *et al.*, 2007). Poor kinetics of dissolved oxygen reduction at the cathode, differing and often unpredictable activity of microbial communities in the anode chamber, high internal resistance arising from proton exchange membranes and separators used in between the anode and the cathode chambers are among the most important parameters limiting the performance of microbial fuel cells (Kim *et al.*, 2007). In the above factors, performance limitation due to high internal resistance has been tackled by using membrane-less microbial fuel cells using separators such as

glass wool (Narayanan *et al.*, 2012). However, in the membrane-less design, crossover of oxygen from the cathode to the anode compartment cannot be precluded completely (Mokhtarian *et al.*, 2013).

Implementing polymer electrolyte membranes with considerably high proton conductivity is a viable alternative. In this regard, a number of polymer membranes capable of conducting protons across the cathode and anode chambers in microbial fuel cell have been reported. Most notable among them are Nafion (a perfluorosulfonic acid based ionomer) and its composites (Rahimnejad *et al.*, 2010). Performance of Nafion membranes depends on their thickness and equivalent weight estimated based on the degree of sulfonation. Thus Nafion 117 and Nafion 112 have been tested successfully as separators and proton conductors in microbial fuel cells. Nafion 117 has excellent chemical stability and proton conductivity but has limitations such as biofouling, oxygen permeability and non-specific transport of cations other than protons (Chae *et al.*, 2008). Recently the performance of Nafion 117 has been compared with another sulfonated polymer electrolyte, SPEEK (sulfonated poly ether ether ketone) (Ghasemi *et al.*, 2013). Composites of polyaniline nanoparticles and Nafion 112 were reported to have lower biofouling and result in nine-fold increase in microbial fuel cell power density compared to pristine Nafion 112 membranes (Mokhtarian *et al.*, 2013). However, the composition of the composite membranes should be carefully controlled which otherwise led to problems related to phase separation (You *et al.*, 2010).

Ionically conducting polymer hydrogel electrolytes could be more attractive owing to their better water retention, ionic conductivity and mechanical flexibility compared to linear polymer membranes. Ionically conducting polymer hydrogels have been previously demonstrated as electrolytes for supercapacitors (Choudhury *et al.*, 2006) and as electromechanical actuators in artificial muscles (Haider *et al.*, 2007). We report here for the first time, the application of partially hydrolyzed polyacrylamide hydrogels and their nanocomposites with multi-walled carbon nanotubes as solid electrolytes for microbial fuel cells. Carbon nanotubes are introduced into the gel matrix to improve their mechanical stability and provide regular proton conduction channels in the matrix (Gunavathi *et al.*, 2012; Kannan *et al.*, 2009). Effect of carbon nanotube loading and processing method on the properties of the composite gel electrolytes are studied for application in microbial fuel cells.

MATERIALS AND METHODS

Materials: Acrylamide, Sodium Dodecyl Sulfate (SDS), ammonium persulfate (APS) and NaOH were obtained from merck. N, N¹-methylene bisacrylamide was purchased from Himedia. TEMED was obtained from sigma.

Methods

Synthesis of MWNT/PAM composite hydrogel: The monomer solution was prepared by dissolving 7.1 g of acrylamide and 1.54 g of N, N¹-methylene bisacrylamide in 100 mL deionised water. Pristine gel was prepared by mixing 10 mL of this monomer solution, 0.1 mL of 10% SDS, 1% APS (1%) and 10 μ L TEMED. Different MWNT/PAM composite hydrogels were synthesized by dispersing different loadings (2, 4, 6 and 10 mg) of MWNT ultrasonically into the monomer solution for 20 min followed by the addition of 0.01 g APS (1%) and 10 μ L TEMED.

Preparation of partially hydrolyzed MWNT/PAM composite hydrogel: Highly cross-linked pristine and MWNT/SDS-PAM composite hydrogels of different MWNT loadings were immersed in 20% (w/v) NaOH solution for 48 h. After immersion, the gels were rinsed with deionised water and dried at room temperature.

Characterization of partially hydrolyzed MWNT/PAM composite hydrogels: The morphology of highly cross-linked partially hydrolyzed pristine and MWNT/PAM composite hydrogels of different MWNT loadings were studied using Scanning Electron Microscopy. Swelling behavior of the composite hydrogels was analyzed using lyophilized samples. Differential scanning calorimetry was performed using DSC Q20 V24.4 Differential Scanning Calorimeter. Ionic conductivity of partially hydrolyzed MWNT/PAM composite hydrogels of varied MWNT loadings were studied using Electrochemical Impedance Spectroscopy. The experiments were performed using a CH Instruments Model 920 C Scanning Electrochemical Microscope.

RESULTS AND DISCUSSION

Figure 1 shows the scanning electron micrographs of the pristine polyacrylamide gel and carbon nanotube/polyacrylamide composite gels after lyophilization. With increasing amounts of carbon nanotubes in the gel matrix, the average pore size increases as observed in the micrographs of pristine gel (Fig. 1a), 0.02, 0.04, 0.06, 0.08, 0.1% (w/v) (Fig. 1b-f, respectively). Mechanical stability of the gels increased with increase in carbon nanotube content as understood from physical examination.

Swelling behavior of the hydrogels was studied to understand the dimensional stability of the hydrogels under the operational conditions of the fuel cell. The weights of the partially hydrolyzed lyophilized, pristine and MWNT/PAM hydrogels were noted and were allowed to swell in deionised water at room temperature. Samples were removed from the water at periodic intervals and weighed after gently blotting excess water from the surfaces. The % swelling ratios were calculated from the following expression (Haider *et al.*, 2007):

$$\text{Swelling ratio(\%)} = \frac{W_w - W_d}{W_d} \times 100$$

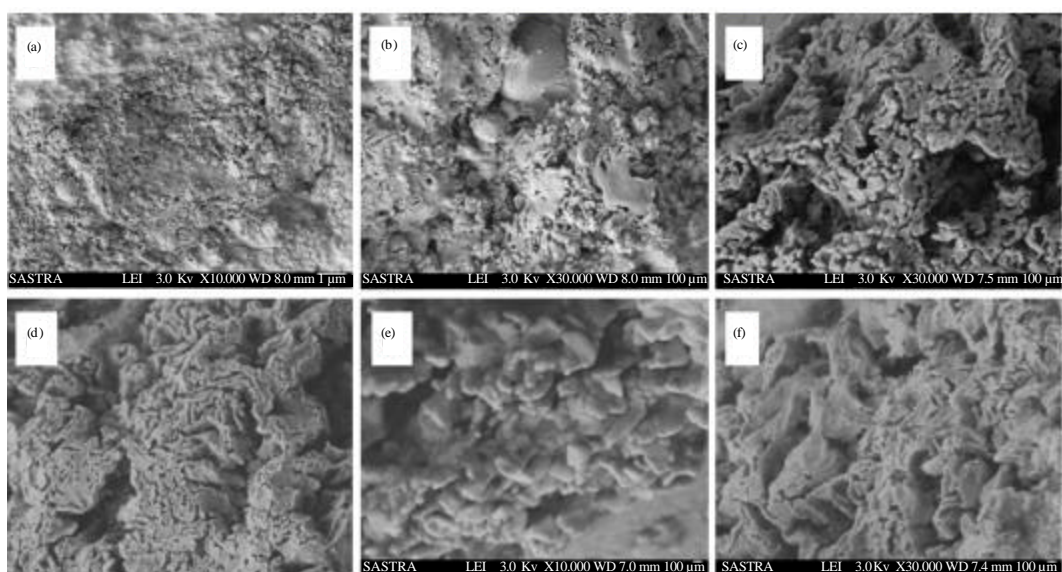


Fig. 1(a-f): Scanning electron micrographs of partially hydrolyzed lyophilized, (a) pristine polyacrylamide gel and MWNT/PAM composite gels with different MWNT loadings, (b) 0.02%, (c) 0.04%, (d) 0.06%, (e) 0.08% and (f) 0.01%

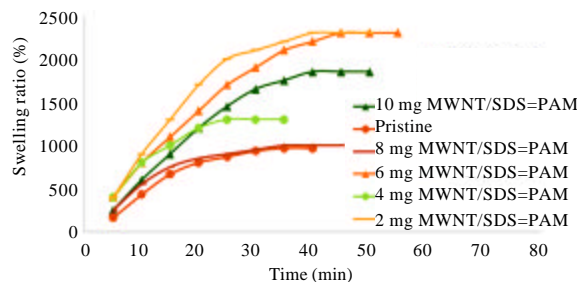


Fig. 2: Swelling curves of partially hydrolyzed pristine and MWNT/polyacrylamide hydrogels

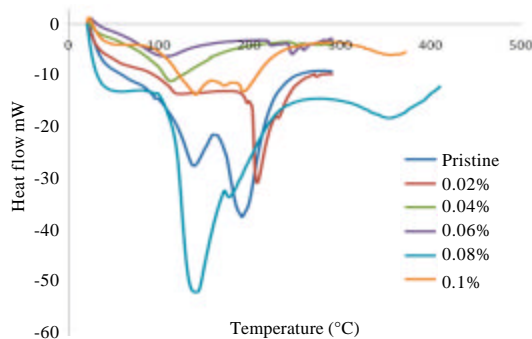


Fig. 3: Differential scanning calorimetry data of partially hydrolyzed pristine and MWNT/polyacrylamide hydrogels

The corresponding swelling curves are shown in Fig. 2. The swelling capacity indicated by the amount of water uptake, of the lyophilized partially hydrolyzed MWNT/PAM composite hydrogels was found to be more than pristine gels due to the increase in flexibility of the gel.

More specifically, 0.02, 0.04 and 0.06% (w/v) MWNT/PAM composite gels were found to have higher swelling capacity than pristine gel due to the increase in flexibility of the composite gels. Composite gels containing 0.08% (w/v) MWNTs show similar swelling capacity as the pristine gel. On the other hand, composite gels containing 0.1% (w/v) MWNTs were found to have higher swelling capacity than that of the pristine hydrogels hydrolyzed partially to the same extent. 0.08% loading of MWNTs could be considered as the threshold limit of MWNT loading in the cross-linked polyacrylamide hydrogel. Addition of more MWNTs to the gel matrix probably results in more heterogeneity and microphase separation of the polymer and nanotube phases thereby reducing its dimensional stability.

Further, in order to understand the glass transition behavior and crystallinity of the gels, Differential Scanning Calorimetry (DSC) was performed on the pristine and the composite gels. Figure 3 shows the DSC plots of the pristine and the composite gels. The glass transition temperature (T_g) was found to decrease with increasing MWNT content in the composite gels from pristine to 0.06% MWNT. The decrease in T_g could be explained in terms of increase in flexibility of the polymer chains arising from the introduction of carbon nanotubes into the gel matrix. This result is also in accordance with the swelling studies which indicated an increase in swelling capacity from pristine to 0.06% MWNT. In addition, the 0.08% MWNT/PAM composite gel has a

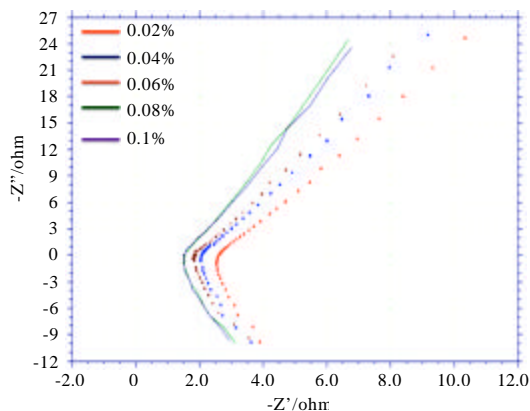


Fig. 4: Electrochemical impedance spectra (Nyquist plots) of partially hydrolyzed pristine and MWNT/polyacrylamide hydrogels

similar T_g as pristine indicating similar crystallinity. Also, in accordance with the swelling data, the 0.1% MWNT/PAM composite gel has a higher T_g than pristine gel due to heterogeneity and phase separation.

After understanding the morphology, swelling behavior and thermal properties of the composite gels, proton conductivity was analyzed using electrochemical impedance spectroscopy by sandwiching the partially hydrolyzed polyacrylamide hydrogels between two parallel metal plates. The Nyquist plots (imaginary vs. real impedance) are shown in Fig. 4. Proton conductivity of the gels was calculated from the intercept of the impedance plot at the real impedance axis of the Nyquist plot and was found to increase with increase in MWNT content from pristine to 0.08% MWNT. The proton conductivity of 0.1% MWNT was found to be similar to that of 0.08% MWNT. Thus, the MWNT/PAM composite gels could be used as solid state proton conductors in microbial fuel cells.

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