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Synthesis of sulfonated poly(ether ether ketone)/layered double hydroxide nanocomposite membranes for fuel cell applications

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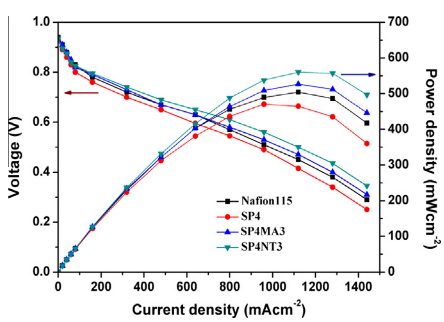
HIGHLIGHTS

- SPEEK–LDH composite membranes were prepared using two varieties of LDH.
- Both LDHs enhanced the water uptake and proton conductivities.
- Mg–Al LDH composite shows higher proton conductivities than that of Ni–Ti LDH.
- The maximum peak power density of 560 mW cm^{-2} was achieved at 80 °C and 100% RH.

GRAPHICAL ABSTRACT

The presence of LDH in the SPEEK–LDH membranes enhances the single cell performance.



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ABSTRACT

Sulfonated poly(ether ether ketone) (SPEEK) can be a potential replacement of Nafion owing to its cost effectiveness and tunable sulfonation sites. The proton conductivity of SPEEK can be improved by increasing the degree of sulfonation (DS) but at the cost of sacrificing its mechanical properties. The presence of the inherited structural water in layered double hydroxide (LDH) can be highly beneficial in improving the proton conductivity of the nanocomposite membranes. SPEEK–LDH composite membranes were prepared using two varieties of LDH and characterized by FT-IR, TGA and proton conductivity measurements. The thermal stabilities of the SPEEK–LDH composite membranes increase with increasing LDH content. The proton conductivity and peak power density of the SPEEK–LDH composite containing 3 wt.% LDH have been found to be 229.6 mS cm^{-1} and 560 mW cm^{-2}, respectively, compared to 147.6 mS cm^{-1} and 470.4 mW cm^{-2}, respectively for SPEEK at 80 °C and 100% relative humidity.

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1. Introduction

Fuel cells have received considerable attention as an alternative green technology of power source which can partially solve the energy crisis issues, global warming, environmental pollution and rapid depletion of the fossil fuel. Fuel cells are electrochemical devices those convert chemical energy directly to electrical energy using fuels such as hydrogen, methanol, natural gas. Fuel cells possess several advantages such as environmental friendliness, high efficiency and simplicity [1–3]. Fuel cell, specifically polymer electrolyte membrane fuel cell (PEMFC) consists of a polymer membrane that separates anode and cathode and helps in conducting proton from the anode to the cathode. Nafion is considered to be the most widely used electrolyte membrane for PEMFC owing to

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their high proton conductivity, chemical stability and durability. However, the low proton conductivity at high temperature (>80 °C) and at low humidity conditions, along with its cost makes Nafion unsuitable for practical applications [3–4]. Hence, several approaches and new membrane materials have been devised to avoid the demerits of Nafion [4–8].

Sulfonated poly(ether ether ketone) (SPEEK) is one of the inexpensive non-perfluorinated polymer, having high mechanical, chemical and thermal stability [9–11]. The sulphonic groups are introduced into the polymer backbone to facilitate enhanced water retention property and proton conductivity of the membrane. Inorganic nanofillers such as titanium dioxide (TiO_2), heteropoly-acid, layered double hydroxide (LDH), zirconium oxide and phosphomolibdic acid (ZPMA), nanoclay and silica nanoparticles have been added to SPEEK membranes to further enhance its water retention and mechanical property [5,11–17].

LDH ($Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$), also known as hydrotalcite, have been widely investigated and studied and used extensively for many applications such as catalysts, ceramic precursors adsorbents due to their physicochemical properties. LDHs are structurally similar to brucite [$Mg(OH)_2$] and a class of nano-sized anionic clay family. LDH may be generally represented by the chemical structure $[M^{2+}_{1-x}M^{3+}{}_x(OH)_2]^{x+}[A^{n-}{}_{x/n}]_nH_2O$, where M^{2+} is a divalent metal cation including Mg^{2+}, Fe^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+} and M^{3+} is a trivalent metal cation including Al^{3+}, Cr^{3+}, Ga^{3+}, Fe^{3+} and Ni^{3+}. A^{n-} is an anion such as CO_3^{2-}, NO^{3-}, SO_4^{2-}, OH^-. In this structure, positively charged divalent metal cations can be replaced with trivalent metal cations. A^{n-} is exchangeable nitrate ions for maintaining charge neutrality in the structure. LDH sheets are stacked with each other and are held by weak interactions through hydrogen bonding [18–22]. Addition of LDH to SPEEK have been found to increase the thermal stability and permeability and proton conductivity of the SPEEK and decrease the diffusion coefficient compared to Nafion [11,23–25]. LDH particles consist of structural water in their surface and interlayer and are anticipated to transport protons in their composites more effectively than the virgin membranes. In contrast, Lee et al. [23,24] have reported a decreased ion conductivity and diffusion coefficient for Nafion-LDH composite compared to virgin Nafion.

In this work, two varieties of LDH particles have been synthesized and incorporated into SPEEK membrane and studied their physico-mechanical properties. In order to confirm the effect of the LDH on the conductivity of the membranes, these LDHs have also been incorporated into Nafion and their proton conductivities have been investigated.

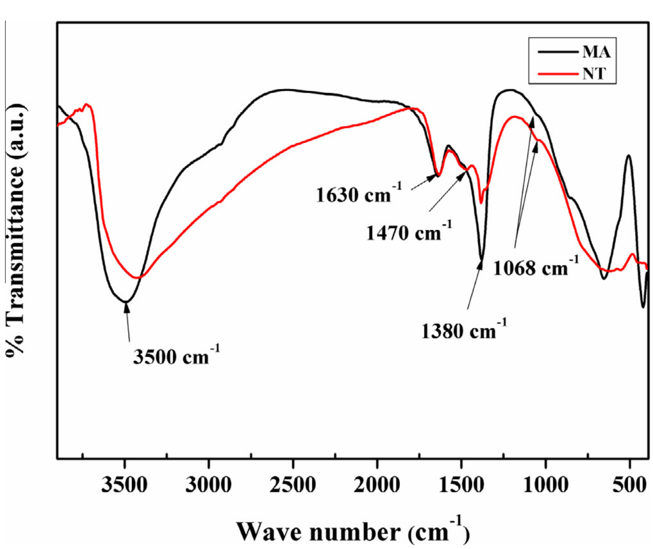

Fig. 1. FT-IR curves of MA and NT LDH.

2. Experimental

2.1. Materials

Poly(ether ether ketone) (PEEK, Victrex 450 PF powder), sulfuric acid, dimethylacetamide (DMAc), magnesium nitrate, aluminum nitrate, sodium hydroxide, sodium carbonate, nickel nitrate hexahydrate and titanium tetrachloride were purchased from Sigma Aldrich, Germany.

2.2. Preparation of the SPEEK

Sulfonation of PEEK to prepare SPEEK was similar to the procedure reported earlier [2]. PEEK was completely dried in a vacuum oven at 100 °C to remove moisture prior to its use. Then the desired amount of PEEK powder was dissolved in sulfuric acid (95%) in a three-neck round bottom flask under nitrogen atmosphere with vigorous stirring at 55 °C for 4 and 6 h to prepare SP4 and SP6, respectively. The solution was then precipitated in a large excess of ice-cold water under stirring condition. The polymer precipitate was washed several times with deionized water until neutral pH. The polymer was finally dried in a vacuum oven at 70 °C for overnight.

2.3. Preparation of layered double hydroxides (LDH)

LDH was synthesized using similar procedure as described in the literature [26–27]. Mg–Al-based LDH (MA) was synthesized by following method. Sodium carbonate (0.025 mol) and sodium hydroxide (0.2 mol) were dissolved in 100 ml deionised (DI) water under stirring followed by the slow addition of 100 ml aqueous solution of magnesium nitrate ($Mg(NO_3)_2{\cdot}6H_2O$) 0.075 mol and aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$) 0.025 mol. Then small amount of additional 1 M NaOH solution was added to maintain the pH at 8–9, as a result, the required LDH precipitates out. The white precipitate was aged at 75 °C for 24 h and then filtered and continuously washed with DI water until pH 7. The obtained solid was then dried in a vacuum oven at 80 °C for 24 h. Similarly, urea method was followed for the synthesis of Ni–Ti-based LDH (NT) as described by Zhang et al. [27].

2.4. SPEEK/LDH membrane fabrication

A calculated amounts (1, 3, 5 wt%) of LDHs (MA or NT) were dispersed in DMAc solvent and sonicated for 15 min. Then it was mixed with SPEEK solution in DMAc solvent. The mixture was stirred and sonicated for half an hour and then cast onto a petri-dish. The solvent was then evaporated in a vacuum oven at 70 °C. The prepared nanocomposites are designated as SPxyz, where, x is the reaction time (4 or 6 h), y is the types of LDH (MA or NT) and z is the wt% of LDH.

3. Characterization

Fourier transform infrared (FTIR) studies were performed using a Nicolet 6700 spectrometer (Thermo Scientific, USA) at room temperature over a frequency range of 4000–400 cm^{-1}. Wide-angle X-ray diffraction (WXRD) studies of MA and NT were performed at room temperature on a D/Max 2500 V/PC (Rigaku Corporation, Japan). The H NMR spectra was used to determine the degree of sulfonation of poly(ether ether ketone) using 400 MHz FT/NMR spectrometer (JNM-EX400, JEOL Ltd, Japan). The H NMR sample was prepared by dissolving of SPEEK polymer in a dimethyl sulfoxide (DMSO). The water uptakes of the membranes were calculated by measuring the change in the weight between the dry and

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