



Antioxidant proton conductive toughening agent for the hydrocarbon based proton exchange polymer membrane for enhanced cell performance and durability in fuel cell



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HIGHLIGHTS

- SPEEK65/Ce/OSPN proton exchange membrane was fabricated via sol-gel reaction.
- SPEEK65/Ce/OSPN showed higher conductivity than pristine SPEEK65 membrane.
- SPEEK65/Ce/OSPN showed even superior chemical stability to pristine SPEEK65.
- SPEEK65/Ce/OSPN showed higher peak power density than pristine SPEEK65.

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ABSTRACT

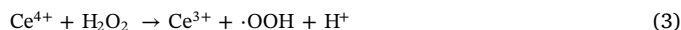
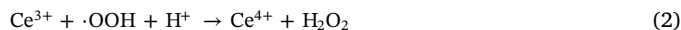
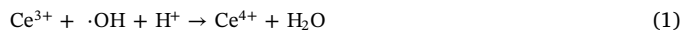
The antioxidant toughening agent for the hydrocarbon based proton exchange polymer electrolyte membranes, cerium/organosiloxane polymer network (Ce/OSPN), is synthesized via sol-gel reaction. Ce/OSPN is introduced to the sulfonated poly(ether ether ketone) (SPEEK), a typical hydrocarbon type polymer electrolyte membrane, by formation of a semi-interpenetrating polymer network (semi-IPN) structure. As Ce/OSPN possesses superior properties to SPEEK in mechanical flexibility, proton conductivity, and oxidation stability than SPEEK, it resolves 3 inherent drawbacks of the pristine SPEEK membrane including (i) brittleness, (ii) low proton conductivity, and (iii) poor durability. Addition of 20 wt% Ce/OSPN (at Ce/silicon mol ratio = 0.10) enhances the elongation at break of the SPEEK membrane about twice. The power density of the MEA fabricated with the semi-IPN membrane is 208 mW cm^{-2} , which is much higher than that of the pristine SPEEK membrane, 165 mW cm^{-2} . The power density loss of the same semi-IPN membranes as determined by the Fenton's test is 4.8%, whereas those of pristine and semi-IPN membrane without cerium are 33.9% and 34.0%, respectively. This Ce/OSPN agent is expected to be applied to a variety of hydrocarbon based polymer electrolyte membranes.

1. Introduction

Many researchers have been developing a variety of hydrocarbon (HC) type proton exchange membranes to replace the commercial perfluorinated sulfonic acid (PFSA) ones such as Nafion series from Dupont [1–5]. The typical HC type electrolyte membranes include sulfonated poly(arylene ether sulfone) (SPAES), sulfonated poly(arylene ether ketone) (SPAEK), sulfonated polyimide (SPI), and sulfonated poly(ether ether ketone) (SPEEK) [6–11]. The advantage of HC type membrane has cost-effectiveness, significantly low fuel permeability, and superior mechanical and thermal stability. HC based membranes, however, are quite difficult to obtain the phase separation as distinctively as PFSA membranes because of its rigid rod-like main

chain structure, thereby limiting the improvement in proton conductivity. In addition, the HC type electrolyte membranes have poor durability because of polymer degradation caused by hydrogen peroxide or hydroxyl radical attack [12–16]. Therefore, improving the durability as well as brittleness and proton conductivity in HC type membranes is urgent for their commercialization.

As a previous strategy for mitigating the degradation of the HC type membrane, radical scavenging additives were placed in the membrane.



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Cerium ion or cerium oxide is a typical additive. Ce^{3+} inside the electrolyte membrane is oxidized to Ce^{4+} , and the hydroxyl radicals are reduced to water molecule. Conversely, when Ce^{4+} is reduced to Ce^{3+} , hydrogen peroxide is oxidized to oxygen. As described above, the degradation of the electrolyte membrane can be mitigated because of the radical scavenging effect by cerium redox reaction [17–20]. In fact, excellent long-term operational stability with HC and PFSA membranes containing cerium has been determined by the accelerated stress test [21–25]. However, the cerium composite membrane system has two disadvantages: (i) the inactivation of the ion conduction group by the cerium ion. The cerium ions in the ion cluster exchange with the proton of the sulfonic acid group to reduce the ion cluster size, thus decreasing the proton conductivity and the cell performance [19,22,26] (ii) cerium ions are very mobile in the operating state of the fuel cell and thus easy to flow out of the membrane by diffusion process. Additional movement of ions also possibly takes place by current flow [27–32].

The cerium ions outflowed from the membrane may escape into the drain water or may remain in the electrode layer. If the cerium ions remain in the electrode layer, the activity of the oxidation and reduction reactions created by hydrogen and oxygen in anode and cathode is quite reduced, thus deteriorating the cell performance [27]. In order to realize the long-term effect of radical scavenging, a new method that can fix radical scavenger inside the membrane is needed.

Meanwhile, the HC type polymer/organosiloxane polymer network (OSPN) membranes have been studied in our laboratory. The composite membranes using OSPN system have more flexible mechanical properties of the membrane using rubbery material 3-glycidyloxypropyltrimethoxysilane (GPTMS) to improve the brittle mechanical property. The 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) was added to enhance the proton conductivity [28,29,33]. However, the durability of the HC type OSPN composite membranes has not been investigated. In this study, a multifunctional antioxidant system was prepared to resolves the three weaknesses of the HC type membranes mentioned above. The radical scavenger such as cerium isopropoxide (cerium precursor) was fixed into OSPN structure composed of GPTMS and HEDPA through hydrolysis and metal-alkoxy reaction. The radical scavenging effect may be realized for a long time by fixing radical scavenger into OSPN structure to prevent from leaching out. Furthermore, the system simultaneously may improve the brittleness and proton conductivity, which are the general disadvantages of HC type membranes. Cerium embedded OSPN (Ce/OSPN) synthesized by sol gel reaction was added to sulfonated poly(ether ether ketone) (SPEEK) membrane in semi IPN structure. SPEEK (degree of sulfonation: 65%) was used as the model HC type polymer matrix because of its low cost, good thermal stability and easy to synthesize. In order to analyze the structure of this semi-IPN membrane and the degree of additive dispersion, elemental analysis was measured by scanning electron microscopy/energy-disperse X-ray spectroscopy (SEM/EDS). The water uptake, proton conductivity, and mechanical properties were analyzed to investigate the physical properties of the composite membranes. The Fenton's test was carried out under the Ex-situ condition, and the unit cell performance test was conducted to determine the effect of radical attack on membrane-electrodes assembly (MEA) performance.

2. Experimental

2.1. Materials

Poly(ether ether ketone) (PEEK, Mw 100,000 g mol⁻¹, ICI Company, Rotherham, UK), sulfuric acid (Duksan Reagents & Chemicals, Korea), and N,N-dimethyl acetamide (DMAc) (Sigma-Aldrich, St.Louis, MO, USA) were used to prepare sulfonated poly(ether ether ketone) (SPEEK). GPTMS and HEDPA were purchased from (TCI, Tokyo, Japan) and used to synthesize the organosiloxane networks. Cerium (IV)

Table 1

EDS elemental analysis of SPEEK65/0.10/20% membrane.

Element	Surface		Cross-section	
	Weight (%)	Atomic (%)	Weight (%)	Atomic (%)
C K	63.98	73.51	63.65	73.29
O K	25.69	22.16	25.80	22.30
Si K	1.67	0.82	1.77	0.87
P K	3.57	1.59	3.56	1.59
S K	4.28	1.84	4.31	1.86
Ce L	0.81	0.08	0.91	0.09
Totals	100.00	100.00	100.00	100.00

isopropoxide, Ce 37–45% (CeOR_x), (Alfa Aesar) was used as cerium oxide precursor. Pt/C (40 wt.%) were purchased from Alfa Aesar (Alfa Aesar, USA), and Nafion[®] solution(5 wt.%) from CNL Energy (Korea) were used as catalyst binder.

2.2. Sulfonation of PEEK

PEEK (5 g) was dissolved in 100 mL of sulfuric acid (95%). The resulting polymer solution was stirred in a three-neck flask under nitrogen at 35 °C for 15 h. After the completion of the reaction, the polymer solution was dropped into de-ionized water. The resulting precipitate was collected and washed with de-ionized water several times. The final product, sulfonated PEEK (SPEEK), was dried at 100 °C for 1 day.

2.3. Preparation of semi-IPN composite membranes

The SPEEK65/Ce/OSPN semi-IPN composite membranes were prepared using DMAc as the casting solvent. SPEEK65 was dissolved in 10 mL DMAc under stirring until the formation of a homogeneous phase (solution A). The Ce/OSPN was prepared from GPTMS, HEDPA, and Ce (OR)_x. GPTMS (0.235 g) were mixed with DMAc (1 g) and de-ionized water (0.02 g) for hydrolysis and diluted nitric acid (0.5 M) (0.02 g). The solution was stirred for 10 min at room temperature to partially hydrolyse the organosiloxane and completely react with water. A clear sol was formed, to which Ce(OR)_x was added to prepare a series of mixtures with different cerium/silicon (Ce/Si) molar ratios of 0.05, 0.10, 0.15, and 0.20. The mixtures were stirred for 1 h to completely react with Ce(OR)_x with partially hydrolysed organosiloxane. Finally an additional HEDPA (0.346 g) was introduced to complete the hydrolysis of the cerium/organosiloxane composition, along with DMAc (1 g) to adjust the solution concentration to a suitable level for application (solution B). Each solution B was added into solution A to prepare a series of mixtures with different total additive concentrations of 10, 20, and 30%. Each mixture was stirred for 4 h at room temperature and then cast onto a petri dish, followed by curing and drying at 100 °C for 1 day. The semi-IPN composite membranes were obtained after further drying at 130 °C for 3 h under vacuum [34]. The thickness of the membranes prepared is 75–80 μm.

2.4. Characterizations

2.4.1. Elemental analysis

The concentration distribution of sulfur, silicon, phosphor, and Ce in the SPEEK65/0.10/20% composite membrane was analyzed by field-emission scanning electron microscopy (FE-SEM, JEOL, JSM7000F, Tokyo, Japan) and energy dispersive X-ray spectroscopy (EDS, Oxford INCA system, Oxford, UK). X-ray exposure time for EDS was 100 s. The membrane was micro-tomed into several pieces in liquid nitrogen, and the morphology of the surface and cross-section was examined at an acceleration voltage of 30 kV.

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