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Alternative hybrid electrolytes based on a series of bis(trialkoxysilyl)alkanes and 3-(trihydroxysilyl)-1-propane sulfonic acid applied in gas diffusion electrodes of proton exchange membrane fuel cells

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ABSTRACT

This study demonstrates a method for improving the electrolyte distribution in catalyst layers and enhancing the utilization of catalyst existing in primary pores. Bis(trialkoxysilyl)alkanes (BTAS-alkanes) and 3-(trihydroxysilyl)-1-propane sulfonic acid (THS)Pro-SO_3H) precursors have been used to prepare a series of hybrid electrolytes with various organic segment lengths of BTAS-alkanes and ratios of organic moiety and sulfonic acid groups. Investigations of BTAS-alkanes series includes bis(triethoxysilyl)octane (BTES-Oct), bis(trimethoxysilyl)hexane (BTMS-Hex), and bis(triethoxysilyl)ethane (BTES-Eth). Small angle X-ray spectroscopy (SAXS) identifies morphological phase separation in BTES-Oct and BTMS-Hex hybrid electrolytes. The results of mercury porosimetry and BET porosimetry show that the hybrid electrolytes have better capability than Nafion ionomer to penetrate into primary pores of the catalyst layers. Electrochemical measurements including electrode polarization, electrochemical active surface (EAS) and electrochemical impedance spectroscopy (EIS) are discussed. The BTES-Oct or BTMS-Hex hybrid electrolytes with higher ratio of organic moiety and sulfonic acid group have achieved better electrode performance. Oxygen benefit current (OBC) results indicate that higher ratios of BTES-Oct/(THS)Pro-SO_3H provides higher hydrophobicity with better gas transport properties. However, the hybrid electrodes exhibit lower cathode performance than Nafion®-based electrodes due to excessive electrolyte incorporated in the catalyst layer.

1. Introduction

Due to their higher power densities and environmental benefits, proton exchange membrane fuel cells (PEMFCs) have recently generated an enormous amount of research as alternative power sources for automotive, stationary, and portable applications. However, several issues must be addressed before PEMFC systems can be commercialized, including the use of expensive components with limited performance, and the poor durability of membrane electrode assemblies (MEAs). Ironically, low catalyst activity and mass transport limitations at the cathode leads to lower power density values. An optimized MEA configuration that includes a catalyst layer and gas diffusion layers (GDLs) could address these shortcomings [1–3]. MEA efficiency depends on three major factors: (i) amount of catalyst, (ii) type of proton exchange membrane (PEM), and (iii) gas diffusion layers (GDL) characteristics [4]. Among these factors, GDL characteristics play an important role in achieving high performance of PEMFC. The GDL acts as an effective path for the transport of gas reactants to the catalyst layer, exhibiting low electronic resistivity for the transmission of electrons. The GDL also act as a flexible surface with proper hydrophobicity preventing water flooding and providing better contact with neighboring components [5,6]. High PEMFC performance requires an optimal combination of electron transport, proton transport and mass transport [7]. The combination of these mechanisms forms a three-phase-boundary where electrochemical reactions occur [8,9].

One of the important goals in current PEMFC research is to address the basic understanding of both gas transport and ion transport. The transport of gas and ions occurs in different directions; gas diffuses perpendicularly to the ionomer thin film, while ions migrate parallel to it. Electrochemical reactions generally occur in the gas diffusion electrode (GDE). Because these reactions involve complicated factors, it is difficult to evaluate the influence of one parameter while keeping other properties constant. For example, a variation in the ionomer content simultaneously affects gas permeability, catalytic activity and ionic resistance [4–6]. Wilson et al. employed a thin-film method to improve the electrolyte distribution in catalyst layers. This approach enhances PEMFC performance

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by increasing the number of Pt particles in contact with proton conducting networks, which in turn increases catalyst utilization [10–12]. The distribution of the three-phase-boundary is another critical phenomenon governed by the microstructures of catalyst layers. Recent study by Watanabe et al. shows that there are two types of pores in the catalyst layer: primary pores with a diameter of <0.1 μm and secondary pores with a diameter of >0.1 μm and more than 85% of Pt particles are located on the wall of primary pores [13,14]. Uchida et al., further analyzed pore structures in the PEMFC catalyst layer, showed that sulfonated polymer electrolytes could not penetrate into primary pores with small diameters [15,16]. This suggests that the catalyst utilization in primary pores is excluded from three-phase boundaries.

Recent research efforts have focused on the preparation of organic–inorganic hybrids through sol–gel processes [17–19]. These hybrids have the advantages of thermal stability provided by an inorganic backbone, while organic chains confer the required specific properties such as flexibility and processibility. These hybrid electrolytes become proton conducting when they are doped with acidic moieties such as monododecylphosphate (MDP) or 12-phosphotungstic acid (PWA) and a family of acid functionalized polysilsesquioxanes (Si_2O_3) [20,21]. Nishikawa et al. improved PEMFC performance by combining nano-hybrid electrolytes with platinum-loaded carbon blacks [22,23]. Our earlier reports investigate the feasibility of proton conducting hybrid membranes based on SiO_2/PEG (polyethylene glycol) doped with either 4-dodecylbenzene sulfonic acid (DBSA) or PWA as electrolytes in PEMFCs [24]. Continuing this line of research the present study demonstrates the preparation of various gas diffusion electrodes with a series of hybrid electrolytes through a sol–gel process involving BTAS-alkanes and (THS)Pro-SO_3H precursors. Mercury porosimetry and BET porosimetry measurements were performed to examine the variation of pore-size distribution before and after incorporating the hybrid electrolyte in catalyst layer as binder in advance to examine the possibility of utilization of catalysts located in the primary pores. The rational behavior between organic moieties and electrode performance were examined by varying the organic segment length of BTAS-alkane precursors. This study also compares the performance of the electrodes with the hybrid electrolytes and Nafion®. The outcome of these results indicates that the use of alternative organic–inorganic hybrid electrolyte may be advantageous in utilizing catalyst existing in primary pores of gas diffusion electrode.

2. Experimental

2.1. Preparation of electrodes

2.1.1. Hybrid electrolyte-based electrodes

Hybrid electrolytes were prepared via sol–gel process using BTAS-alkane (Gelest Co. Ltd., Japan) and (THS)Pro-SO_3H aqueous solution (Gelest Co. Ltd., Japan) precursors by varying the organic segment lengths of BTAS-alkanes viz., bis(triethoxysilyl)octane, bis(trimethoxysilyl)hexane and bis(triethoxysilyl)ethane with the number of carbon atoms in their organic moieties of 8, 6, and 2, respectively. Scheme 1 presents the structural formulas of precursors. This study adopts the hybrid electrolytes preparation procedure reported in the literature [22]. Pt-CB (Platinum nominally 50% on Carbon Black Alfa Aesar) and (THS)Pro-SO_3H were mixed with constant stirring for 2 h at room temperature. A BTAS-alkane and 2-propanol (>99.8%, Sigma–Aldrich, USA) mixture was added and once again stirred for 30 min. The mixing ratio of Pt:BTAS-alkane:(THS)Pro-SO_3H:water-IPA were 1:A:B:20 by weight. A uniform paste was spread onto commercial gas diffusion layers (Carbon cloth, 15 wt.% wet proofing, microporous layer on single side, type: CeW1S12, HEPHAS energy) with a circular area of 1 cm^2 and Pt loading of 0.5 mg cm^{-2}. The electrodes were dried under 60 °C and rinsed with deionized water before measurement.

2.1.2. Nafion®-based electrodes

Pt-CB and 2-propanol were mixed and until complete dispersion was achieved. Nafion® solution (5 wt.% Sigma–Aldrich, USA) was added this dispersion and again stirred to produce a uniform paste. The mixing ratio of Pt:IPA:Nafion® was 1:30:C [C representing Nafion® content (0.6, 1, 1.34, and 3)]. The paste was spread onto a commercial gas diffusion layer same as the one prepared in section 2.1.1 with a circular area of 1 cm^2 and Pt loading of 0.5 mg cm^{-2} then dried under 60 °C and rinsed with deionized water before measurements.

2.2. Small angle X-ray scattering measurements

A small angle X-ray scattering instrument (PSAXS-USH-WAXS-002, Osmic, USA) was used to determine the microstructures of the organic–inorganic hybrid electrolytes. BTAS-alkane, (THS)Pro-SO_3H and IPA (Sigma–Aldrich, USA) were mixed in equimolar amount at room temperature with constant stirring for 30 min. The aging process conducted at 60 °C and 95% R.H. for 12 h. After drying, the samples were ground into powder for SAXS measurement.

2.3. Porosimetry measurements

The pore-size distribution and the specific pore volume were calculated from an intrusion curve obtained by a mercury pore sizer (Autopore 9520, Micromeritics Corporate, USA). Mercury porosimetry technique could determine the distribution of pore diameter between 300 μm and 3 nm. The volume of mercury (V) penetrated into the pore is measured directly as a function of applied pressure. For mercury porosimetry, shredded hybrid electrolytes weighing 100–200 mg were subjected to an operating pressure of 0.10–60,000 psi. Intrusion of mercury began at a pressure of 0.44 psi.

The specific surface area and the pore volume distribution were also measured from BET porosimetry (Beckman Coulter SA3100, Taiwan). This type of pore sizer could determine the distribution of pore diameter in nanometer range. For BET porosimetry, hybrid electrolytes were crushed into powder weighed 100–200 mg for subsequent outgassing at approximately 150 °C for 2 h before measurement. Nitrogen adsorption/desorption was carried out at −196.15 °C.

2.4. Electrochemical measurements

Electrochemical measurements were conducted by a half-cell system based on a conventional three-electrode cell [25], and a potentiostat (Autolab, PGSTAT30, Eco Chemie, USA) was adopted to evaluate electrode performance. The prepared GDE was mounted on a PTFE holder to form a working electrode. The PTFE holder contained a Pt ring as current collector, and gases were fed from the back of the electrode. The reference electrode and counter electrode were Ag/AgCl and Pt wire, respectively. Scheme 2 shows the construction of the half-cell system. 0.5 M sulfuric acid was used as a liquid electrolyte for this system. When oxygen was fed into the working electrode, it reacted with the protons of sulfuric acid in an oxygen reduction reaction (ORR). Therefore, the proposed design simulated fuel cell cathode. This design can eliminate other variables while achieving the property of a freestanding GDE.

Three electrochemical measurements were used to evaluate the performances of various electrodes with the same catalyst but different electrolytic binder at room temperature. Galvanstatic