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Polymer electrolyte based on chemically stable and highly conductive alkali-doped polyoxadiazole for direct borohydride fuel cell

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ABSTRACT

Solid electrolyte membranes based on alkali-doped poly (4, 4'-diphenylether-1, 3, 4-oxadiazole) were first introduced into direct borohydride fuel cell (DBFC). The membranes, with outstanding thermal and chemical stability, showed comparable ion conductivity to Nafion® 115 in alkaline solution and peak power density of 146 mW cm^{-2} at the temperature of 40 °C. Furthermore, no weight loss was observed after soaking the membrane in 3 M NaOH solution for 10 days, indicating its excellent chemical stability in alkaline conditions. These results revealed the great potential of alkali-doped polymer for DBFC application.

1. Introduction

Direct borohydride fuel cell (DBFC) as one of the clean and efficient energy conversion device fueled with alkaline borohydride (BH_4^-) solution was first demonstrated by Amendola et al. in 1999 [1]. It has been considered as an attractive energy source for portable and mobile applications due to its technical features such as high volumetric energy density (compared to fuel cells with compressed hydrogen), high theoretical open circuit voltage, ambient operating temperature, and so forth [2]. As the key component of DBFC, the polymer electrolyte membrane is used to separate the liquid fuel from the oxidant and transfer OH^- to complete the circuit.

Due to the fact that the borohydride is unstable in neutral and acidic medium, alkaline solution is used in the anodic half-cell of DBFC [2]. Therefore, membranes with good chemical endurance to alkali are regarded as potential candidates for the application. Traditionally, perfluorosulfonic polymers, such as Dupont Nafion® (Na^+ form), are the most commonly used membranes in DBFC due to their excellent chemical stability in alkaline medium. However, the migration of Na^+ ions across the Nafion® membrane from anode to cathode would lower the pH values of the anodic alkaline solution, causing borohydride decomposition [2]. Furthermore, the extremely high cost of Nafion® membranes is adverse to the commercial application of DBFC. Anion exchange membranes could be another choice for its suppressing effect to Na^+ ions migration, while their positively charged groups, such as quaternary ammonium, are prone to decomposition under strong alkaline condition [3]. Therefore, extensive research is focused on exploration of membranes with good chemical stability and OH^- conductivity.

Recently, heteroaromatic polymers such as polybenzimidazole have received wide attention in alkaline hydrogen fuel cell and alkaline direct alcohol fuel cell applications [4–6]. Unlike traditional ion exchange hydrocarbon ionomers, these non-ionic polymers show excellent ion conductivity and preserve high mechanical and chemical stability after alkaline doping. Considering the similar requirements for membranes in DBFC, the alkali-doped heteroaromatic polymers could be very good membrane candidates for DBFC application. In this paper, the alkali-doped poly (4,4′- diphenylether-1,3,4-oxadiazole) (POD-DPE) membrane was selected as a reference and used in DBFC. Membrane properties and DBFC polarization curves were characterized and discussed in detail.

2. Experimental

POD-DPE (Fig. 1(a)) was synthesized via the cyclodehydration reaction of 4, 4′-diphenylether dicarboxylic acid and hydrazine sulphate in poly(phosphoric acid). Detailed procedure has been described elsewhere [7]. The as-prepared polymer was dissolved in N-methyl-2-pyrrolidone (NMP) and stirred for 3 h at 80 °C to form a 3 wt.% solution. The solution was cast onto a glass plate and evaporated at 80 °C for 12 h to obtain the polymer membrane. Subsequently, the membrane was peeled off and soaked in 3 M NaOH solution for a week to obtain alkali-doped POD-DPE (denoted as "aPOD-DPE"). The membrane was washed with deionized water to get rid of the alkaline solution on the surface before tests. The H^+-form Nafion® 115 (denoted as "N 115") was transformed into Na^+-

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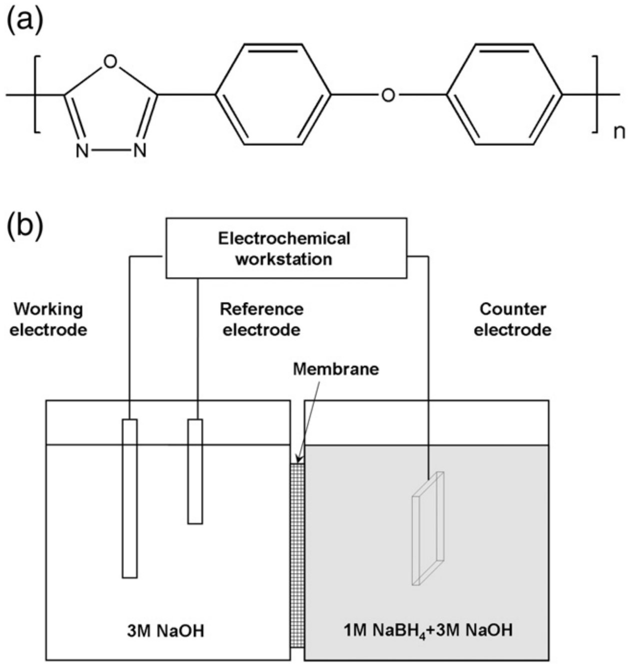

Fig. 1. (a) Chemical structure of POD-DPE; (b) BH_4^- permeability measurement device comprising a diffusion cell and a three-electrode system.

form by soaking in 3 M NaOH at 80 °C for 1 day and washed with deionized water before tests.

TGA measurement was conducted on a Perkin Elmer Pyris Diamond TG/DTA instrument, at a heating rate of 10 °C min^{-1} under N_2 flow. BRUKER DRX400 was used to determine ^1H NMR with dimethyl sulfoxide as solvent and tetramethylsilane as internal standard. The FTIR spectra were recorded on a JASCO FT-IR 4100 spectrometer before and after alkaline doping.

The area resistance of membranes was measured following the method in the previous report [8]: a conductivity cell was separated into two compartments filled with 3 M NaOH solution. The effective area of the cell (S) was 1 cm^2. Electric resistances were measured by electrochemical impedance spectroscopy over a frequency range from 100 kHz to 100 Hz.

The permeability measurement was conducted on a device as shown in Fig. 1(b). At certain time intervals, the concentration of BH_4^- in the left cell was determined via the voltammetric method outlined by Mirkin [9] and Lakeman [10]. A three-electrode cell composed of a gold working electrode, a graphite counter electrode and a mercury/mercury oxide reference electrode was used in the test. The permeability (P) of BH_4^- was calculated via the method described elsewhere [11].

The DBFC single cell fabrication and cell performance evaluation system have been reported previously by our group [12,13]. Pt/C was used as electrocatalyst in both anode and cathode. Pt loadings of cathode and anode were 0.5 mg cm^{-2} and 1 mg cm $^{-2}$, respectively. During the test, 1 M $NaBH_4$ in 3 M NaOH solution was fed to the anode at a flow rate of 0.5 ml min^{-1}. Oxygen was fed to the cathode with the pressure of 0.1 MPa. The cell temperature was kept at 40 °C. The polarization curves were recorded when the cell operated for at least 2 hours to ensure an established balance in the fuel cell process.

3. Results and discussion

Two weight losses are observed from the TGA curve of POD-DPE (Fig. 2(a)). In the region below 150 °C, the weight loss is attributed to the evaporation of absorbed water in the membrane sample. With the increasing temperature, a plateau appears in the range of 150–450 °C, followed by the second weight loss at about 450 °C. This sharp decline corresponds to the decomposition of polymer main chain. According to previous reports [14], incomplete cyclization could possibly occur during the synthesis process, producing residual hydrazide groups. In comparison to the conjugated oxadiazole ring, the hydrazide group is considered to be less stable, and its decomposition occurs in the temperature range of 200–450 °C [15]. Hence it might be beneficial to the stability of the membrane to lower the residual hydrazide content. The POD-DPE polymer with low hydrazide content can be obtained by optimizing the reaction parameter [7]. No distinct weight loss in the range of 200–450 °C verifies that the hydrazide content in the as-prepared polymer is extremely low.

^1H NMR spectrum (Fig. 2(b)) and FTIR (Fig. 2(c)) were used to confirm the polymer structures. From ^1H NMR, the peaks at the chemical shift of 7.3 and 8.2 ppm are assigned to the β-Hs of the ether group (a) and the oxadiazole group (b), respectively [15]. Meanwhile, no obvious signals at 10.7 are found, which correspond to hyrazide protons, further confirming the low content of hydrazide in POD-DPE.

As shown in Fig. 2(c), the absorption bands at 1650–1550 cm^{-1} are contributed to C=N group, which confirmed the formation of characteristic oxadiazole rings during the cyclodehydration reaction. After alkali doping, the absorbance in this region becomes much more intensive, suggesting that hydrogen bonds might be formed between the heterocyclic nitrogen atom and the oxygen atom in dissociated hydroxide. aPOD-DPE shows stronger absorption at 1280–1200 cm^{-1} (C–O–C stretching of the ether group) as well, which is possibly induced by the interaction between ether groups and the alkali. These interactions might facilitate the adsorption and transport of OH^- in the membrane.

The ion conductivity of membranes plays a very important role to determine the performance of DBFC, since the membrane acts as the ion conductor completing the current circuit. Under the actual DBFC operating condition, N 115 conducts Na^+ ions, while alkali-doped membranes conduct OH^- ions [5,6]. Although they possess different ion transport mechanism, their ion conductivities confirmed by the electrochemistry impedance spectroscopy are comparable to finally determine the performance of DBFC. Thus, the feasibility of POD-DPE for DBFC application can be figured out via comparing its ion