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A novel catalyst coated membrane embedded with Cs-substituted phosphotungstates for proton exchange membrane water electrolysis

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ABSTRACT

Catalyst coated membrane (CCM) is the core component of proton exchange membrane (PEM) water electrolysis and the main place for electrochemical reaction and mass transfer. Its properties directly affect the performance of PEM water electrolysis. Aiming at decreasing the polarization loss and the ohmic loss, a novel CCM embedded with Cs_{1.5}HPA in the skeleton of the Nafion[®] ionomer and the Nafion[®] membrane was prepared and possessed functionality of improved protonic conductivity. Meanwhile, the Cs_{1.5}HPA-Nafion ionomer content in the catalyst layers was further optimized. The SEM, EDS and pore volume distribution measurement showed that the Cs_{1.5}HPA embedded in the CCM without agglomeration and the micropore and mesopore were well distributed in the catalyst layer. Furthermore, CCMs were tested in a PEM water electrolyser at 80 °C, beneficial effects on both the Tafel slope and the iR loss were obtained due to the improved protonic conductivity as well as the appropriate pore structure and increased specific pore volume. The performance of the electrolyser cell was obviously improved with the novel CCM. The highest cell performance of 1.59 V at 2 A cm⁻² was achieved at 80 °C. At 35 °C and 300 mA cm⁻², the cell showed good durability within the test period of up to 570 h.

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Introduction

Renewable sources have been utilized via various methods for power generation, but not all the electricity is fed into the grid.

Storage of the excess energy in the form of hydrogen is essential for the realization of large-scale deployment of renewable sources. The method to generate hydrogen on a large scale is the key in hydrogen energy development. So far, among numerous hydrogen production methods, proton

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exchange membrane (PEM) water electrolysis typically operated below 80 °C has been considered as the most promising system due to its advantages such as higher hydrogen purity, greater safety and better reliability [1–3]. However, high energy consumption and cost hinder widespread application of PEM water electrolysis in large scale. The urgent task is to intensify PEM water electrolysis and reduce energy consumption in order to meet the requirement of sustainable hydrogen production.

A characteristic of PEM water electrolysis is the use of CCM where thin and porous catalyst layers are preferably deposited on both sides of the membrane [4,5]. As a core component, the properties of the CCM directly determine the performance of PEM water electrolysis, as the majority of the overpotential that causes the energy loss in PEM water electrolysis is related to the electrochemical process at the anode catalyst layer, where the oxygen evolution reaction (OER) takes place. In addition, the ohmic resistance of the CCM is also a key factor leading to high energy consumption of PEM water electrolysis to give higher current densities. To date most of study is focused on preparing highly active Ir and Ru-based multi-metal oxides or supported catalysts to decrease the OER polarization loss at the anode [6–9]. Concerning the fabricating techniques of the CCM, limited information is available from literatures [10]. At present, the CCM of PEM water electrolysis is fabricated very similar to that of proton exchange membrane fuel cell (PEMFC) [11,12]. Although high performance has been reported by adopting above CCM fabrication method, the most obvious drawback of above CCM is the deficiency of proton transport in the catalyst layers and the membrane which could result in high polarization loss and ohmic loss [13].

To establish proton transport from the bulk of the catalyst layer to the membrane in the CCM, Nafion® ionomer and the Nafion® membrane consisting of perfluorinated sulphonated acid are technically used due to their high protonic conductivity [14]. However, the perfluorinated sulphonated acid could be degraded due to the loss of sulfonic acid ($-HSO_3$) during the OER process which results in the rapidly declining protonic conductivity of the Nafion® ionomer and the Nafion® membrane [6,15,16]. Therefore, both the ionomer and the membrane with improved protonic conductivity and stability are extremely important in the performance improvement and energy consumption decrease of PEM water electrolysis [17,18].

In addition to the demanded proton transport in the CCM, the porous microstructure or the porosity and pore size distribution in the catalyst layer are also of importance [19,20]. Although the addition of ionomer is necessary to maintain the proton transport and act as a binder providing a three dimensional stable catalyst structure in the catalyst layer. The ionomer content in the catalyst layer should be controlled within an appropriate amount. As the ionomers generally form a dense phase and the introduction thereof would thus result in decreased specific active area of the catalyst particles as well as pore structure and pore volume in the catalyst layer [19,21]. It also decreases the electronic conductivity of the catalyst layer [2,28]. A higher pore volume in the catalyst layers is preferred to possess more reaction sites and higher performance. Therefore, efforts that are made to optimize the catalyst layer by adjusting the ionomer content are necessary.

Based on our previous work, $Cs_xH_{3-x}PW_{12}O_{40}$ (hereafter referred to as Cs_x HPA) with the Keggin structure type exhibits high protonic conductivity ($>10^{-2}$ S cm^{-1}) at temperature ranges of 25–80 °C as well as good chemical and thermal stability under water environment [22,23]. In the present study, efforts were made to promote proton transport of the overall CCM. Firstly, both the ionomer and the composite membrane embedded with Cs_x HPA were synthesized and then a novel CCM was developed. Meanwhile, the ionomer content was further optimized in order to achieve an appropriate pore structure and porosity or pore volume in the catalyst layer, which facilitated the oxygen removal and the electronic transport. Finally, PEM water electrolyser cells were assembled and tested for evaluation of the prepared CCMs.

Experimental

Preparation of composite membrane

Firstly, the pretreatment of the Nafion® 212 membrane consisted of sequential immersions of the membrane in 5 wt% H_2O_2 solution (Analytically Pure, Beijing Chemical Factory), distilled water, 0.5 M H_2SO_4 solution (Analytically Pure, Sino-pharm Chemical Reagent Co. Ltd, same for other chemicals unless otherwise specified) and then in distilled water again, at 80 °C for 60 min each step [24].

Based on our previous work [25], the Cs_x HPA with a value of $x = 1.5$ had the highest protonic conductivity. In the following synthesis of the composite membrane and the composite ionomer, only this composition was used and hereafter referred to as $Cs_{1.5}$ HPA. The composite membrane was prepared as follows [26]: firstly, the pretreated Nafion® 212 membrane was immersed into the Cs_2CO_3 solution at 60 °C for 24 h with continuous stirring to substitute H^+ with Cs^+ . The cesium-substituted membrane was labeled as Cs-Nafion 212. Secondly, the Cs-Nafion 212 membrane was treated with phosphotungstic acid solution with a value of $x = 1.5$ under the same conditions. The obtained composite membrane typically contained 5 wt% $Cs_{1.5}$ HPA and hereafter referred to as $Cs_{1.5}$ HPA/Nafion 212. While, the obtained composite membrane contained 10 wt% $Cs_{1.5}$ HPA referred to as $Cs_{1.5}$ HPA (10%)/Nafion 212.

Preparation of $Cs_{1.5}$ HPA-nafion

The composite ionomer was prepared with a modified anchored method [27]. Firstly, a certain amount of Nafion® solution (5 wt%, Dupont) and Cs_2CO_3 aqueous solution were added sequentially into a mixed solution containing 10 mL deionized water and 10 mL ethanol. After magnetic stirring under N_2 for 24 h at 45 °C, phosphotungstic acid was added into the mixed solution dropwise, stirred overnight and then evaporated at 45 °C. The final obtained white colloid solution was labeled as $Cs_{1.5}$ HPA-Nafion. The obtained composite ionomer typically contained 5 wt% $Cs_{1.5}$ HPA.

Preparation of the CCMs

$IrO_2/Sb-SnO_2$ oxide (in mass ratio of 1:1) prepared by Adams method was used as the oxygen electrocatalyst [25,28] and

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