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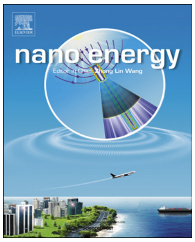

RAPID COMMUNICATION

Integrated inorganic membrane electrode assembly with layered double hydroxides as ionic conductors for anion exchange membrane water electrolysis

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Abstract
In this work, we report a novel integrated inorganic membrane electrode assembly (I^2MEA) for anion exchange membrane (AEM) water electrolysis by using inorganic Mg-Al layered double hydroxides (Mg-Al LDHs) as an ionic conductor. Mg-Al LDHs synthesized by a two-step approach exhibit high hydroxide ion conductivity and superior stability. The resultant ionic conducting nanoparticles are cold-pressed to form a membrane and mixed with a non-precious electrocatalyst to form the catalyst layer onto each side of the membrane. As such, an I^2MEA is formed and used in a water electrolysis setup. It is shown that the present water electrolysis results in a maximum current density of 208 mA cm^{-2} with 0.1 M NaOH as the electrolyte and a cutoff voltage of 2.2 V at 70 °C. More impressively, using 0.1 M Na_2CO_3 as the electrolyte, the I^2MEAs can continuously electrolyze at 80 mA cm^{-2} for 600 hours with a decay rate of as low as 100 μV h^{-1}. This superior stability is attributed to the integrated structure that allows hydroxide ions to transport smoothly.

Introduction

Hydrogen is a viable energy carrier of renewable and sustainable energy and can be generated from low-temperature water electrolysis, which is a promising energy conversion technology for intermittent electricity generated from solar cells and wind turbines [1-3]. Water electrolysis can be generally classified into two categories: alkaline liquid electrolyte water electrolysis and proton exchange membrane (PEM) water electrolysis [4-6]. Alkaline liquid electrolyte water electrolysis has been extensively applied in mass production

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of hydrogen due to its employment of non-precious metals as the electrocatalysts for hydrogen and oxygen evolution reaction [7-10]. However, the concentrated alkaline solutions adopted as the electrolyte are highly corrosive to devices and sensitive to carbon dioxide from ambient air. Furthermore, the management of liquid plant is complex due to its unbalanced plant pressure in the case of intermittent power operation [6]. For the PEM water electrolysis system, it possesses several advantages over alkaline liquid electrolyte water electrolysis, such as a high energy efficiency and compact design due to the use of a solid-state membrane electrolyte [11,12]. However, the acidic environment limits the types of catalysts that can be used to precious metals such as Pt and Ir, which significantly increases the capital cost of this system [13-18]. Thus, both systems have limitations that need to be improved upon for large-scale viability.

In a recent publication, Xiao et al. [19] and Leng et al. [20] have performed some pioneering work in a novel type of water electrolysis, that is, anion exchange membrane (AEM) water electrolysis. In AEM water electrolysis, the AEM and non-precious electrocatalysts can be respectively replaced with PEM and precious electrocatalysts, bringing the following advantages. First, unlike alkaline liquid electrolyte water electrolysis, weak alkaline solutions and even pure water can be used in AEM water electrolysis. This important change facilitates system maintenance and alleviates the corrosion issue. Second, non-precious electrocatalysts can be used in weak alkaline or neutral solution, which thus reduces capital investment and operating costs. Finally, AEM water electrolysis shows a high energy efficiency due to its compact structure.

At present, however, the issue associated with AEM water electrolysis is the low performance of AEMs in terms of hydroxide ion conductivity and chemical stability. Currently, state-of-the-art AEMs possess hydroxide ion conductivities ranging from 10^{-3} to 10^{-2} $\mathrm{S\,cm^{-1}}$, which is not adequate for practical applications [21-23]. Most of AEMs also undergo the following synthesis processes: chloromethylation or bromomethylation, quaternization and alkalization, which are complicated and time-consuming. During the synthesis process of AEMs, the involvement of highly toxic and carcinogenic reagents, such as chloromethylether and trimethylamine, is required and the extent of quaternization is difficult to control [24-27]. Moreover, another challenge for developing AEMs is the poor stability of the functional groups, which are easily degraded by the induction of hydroxide ions through a nucleophilic substitution and/or Hoffmann elimination. Therefore, it is necessary to address the conductivity, stability, and toxicity issues of AEM during the preparation process.

In a recent study, hydroxide ions were successfully conducted using layered double hydroxides (LDHs), a type of inorganic material [28-31]. The LDHs with several cations and inorganic anions have been tested hydroxide ion conductivity at different temperatures and different levels of relative humidity [29,32,33]. The results show that these LDHs have superior stability in alkaline media and acceptable hydroxide ion conductivity. More importantly, the synthesis process is not only simple but also eliminates the use of toxic and carcinogenic reagents. Up to now, however, LDHs have not been used as a hydroxide ion conductor in the AEM water electrolysis.

Herein, in the present work, we report a novel, durable, and low cost AEM water electrolysis design, which employs an integrated inorganic membrane electrode assembly (I^2MEA) using Mg-Al layered double hydroxides (Mg-Al LDHs) as the hydroxide ion conductor in the membrane and catalyst layers. The effects of structural and operating parameters on the performance, including the membrane thickness, electrolyte, and operating temperature, were studied in the AEM water electrolysis setup. The stability of this setup was also determined by a constant-current electrolysis process.

Experimental section

Materials and synthesis of Mg-Al LDHs

All the chemicals were purchased from Sigma-Aldrich and used as received. The platinum group metal (PGM) free Acta 3030 oxygen evolution reaction (OER) catalyst and PGM-free Acta 4030 hydrogen evolution reaction (HER) catalyst were obtained from Acta S.p.A. The anode and cathode gas diffusion layers, nickel foam and carbon paper were purchased from Hohsen and E-TEK, respectively. Mg-Al LDHs were synthesized using a two-step approach, that is, co-precipitation process and then hydrothermal process. Briefly, 0.6 M Mg $(NO_3)_2$ and 1 M Al $(NO_3)_3$ with a mole ratio of $Mg^{2+}/Al^{3+}=3$ were mixed by a magnetic stirrer. 50 mL of the mixture was immediately added into 0.15 M NaOH aqueous solution (200 mL) under vigorous stirring. The nitrogen gas (high-purity) was blanketed in the flask during the synthesis process to prevent the influence of carbon dioxide from the atmosphere. After stirring for 30 minutes, an LDH slurry was made by applying centrifuge separation and washing with deionized (DI) water twice. The slurry was then dispersed into 200 mL of DI water and transferred into an autoclave and hydrothermally treated at 100 °C for 24 hours. The Mg-Al LDHs particles were collected by centrifugation once the reaction time has finished. The precipitates were then washed with DI water several times and dried at 80 °C. The Mg-Al LDH nanoparticles were mechanical ball milling with a ball miller to obtain fine powers. To investigate the influence of precursors on the crystal structure, a mixture of $MgCl_2$ and $AlCl_3$ with the same mole ratio was also prepared to synthesize the Mg-Al LDHs.

Physical characterization

TEM images were obtained by a high-resolution JEOL 2010F TEM system with a LaB_6 filament at 200 kV. The samples were dispersed in ethanol under sonication and dropped on the holey carbon-coated Cu grids. The X-ray diffraction (XRD) patterns of the samples were analyzed with a Philips high resolution X-ray diffraction system (model PW 1825) using a Cu Kα source operating at 40 keV with a scan rate of $0.025^\circ\,s^{-1}$. Surface morphologies of the cross-section of MEAs were determined by scanning electron microscopy (JEOL-6390). SEM-EDX mapping was operated at 15 kV. Brunauer, Emmett, and Teller (BET) analysis using the nitrogen adsorption method (COULTER SA3100) was employed to analyze the surface area of Mg-Al LDH nanoparticles.