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 (I²MEA) 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 electro-catalyst to form the catalyst layer onto each side of the membrane. As such, an I²MEA 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\(_2\)CO\(_3\) as the electrolyte, the I²MEAs 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.

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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.
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 $10^{-2}$ 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 chloromethylthelyer and tri-methylamine, 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 (I2MEA) 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, coprecipitation process and then hydrothermal process. Briefly, 0.6 M Mg (NO3)$_2$ and 1 M Al (NO3)$_3$ 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 K$_\alpha$ source operating at 40 keV with a scan rate of 0.025 °/s. 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, Emmet, and Teller (BET) analysis using the nitrogen adsorption method (COULTER SA3100) was employed to analyze the surface area of Mg-Al LDH nanoparticles.
Fabrication of integrated MEAs

The preparation of Mg-Al LDH membranes by cold pressing method and the ionic conductivity measurement of the membranes were described in the supporting information in detail. Thereafter, the I2MEAs were prepared by the following process: (1) The electrode slurry was prepared by mixing non-precious catalysts with Mg-Al LDHs, PTFE solution and ammonium bicarbonate which were applied as the pore-forming additive; the weight ratio of catalyst, Mg-Al LDHs, PTFE and pore-forming additive was controlled with 50%: 20%: 10%: 20%. The chemical compositions for anode catalyst (OER) and cathode catalyst (HER) are CuCoO, mixed oxides and Ni/ (CeO2-La2O3)/C, respectively. (2) The extra solvents (ethanol and water) were evaporated at 50°C to obtain a black, viscous slurry. (3) The slurry was cautiously transferred to the surface of as-prepared Mg-Al LDH membranes and hot-pressed at 70°C, during which ammonium bicarbonate was volatilized leaving porous structures. The hot-press was maintained at a pressure of 120 kg cm−2 for 15 minutes. The loadings of anode catalysts and cathode catalysts were controlled with 40 mgcat cm−2 and 40 mgcat cm−2, respectively.

Water electrolysis test

A home-made water electrolysis setup was employed to evaluate the performance and durability of the I2MEA. The electrolysis setup includes two titanium end plates, on which a circular serpentine channels with a diameter of 20 mm was machined. The polarization curves and durability tests of I2MEA were measured with an electric load system (BT2000, Arbin Instrument, Inc.). All the I2MEAs were activated by operating the cell at the voltage of 2.0 V for 30 minutes. Polarization curves were then collected by applying a current staircase with a duration of 10 minutes at each current. To determine the operating durability of the I2MEA, a constant water electrolysis was performed at a constant current of 80 mA cm−2. The cell voltage as a function of test time was then recorded. The cell resistance at a frequency of 1 kHz was measured with a potentiostat (EG&G Princeton, model M273) during the electrochemical testing. The electrolytes were supplied by a peristaltic pump at a constant flow rate of 2 ml min−1. The cell temperature was maintained by an electric heating rod and measured by a thermocouple placed near the anode and cathode current collectors.

Results and discussion

The crystal structure of LDHs with the formula (Mg0.667Al0.333)(OH)2(CO3)0.167 0.5H2O is presented in Fig. 1, which shows a rhombohedral structure where each unit has a host layer and an interlayer [34]. The host layer consists of octahedra of Mg2+ coordinated to shared hydroxyl edges, while a part of Mg2+ is substituted by Al3+, generating a positively charged layer. The positive charge is compensated by the carbonate anions located in the interlayer region. Meanwhile, the water molecules can be crystallized or simply intercalated in the free space of this interlayer. It is generally recognized that the intercalated anions and the water molecules within the interlayer play an important role in the hydroxide ion conduction [32]. Here, the as-synthesized Mg-Al LDH nanoparticles by a two-step approach, that is, co-precipitation and then hydrothermal treatment, are shown in Fig. S1. A typical TEM image of Mg-Al LDH nanoparticles is presented in Fig. 2a. It is seen that the Mg-Al LDHs exhibit morphologies of relatively uniform and thin hexagonal-platelets, with the lateral size ranging from 60 to 100 nm (Fig. S2). The ratio between Mg and Al in the samples measured by ICP-AES is 1.98 ± 0.09, close to the theoretical ratio of 2. We also synthesized Mg-Al LDHs by varying the precursors with different anions. Typical TEM images are shown in Fig. S3, demonstrating that as-synthesized Mg-Al LDHs with different precursors have similar morphologies. The high-resolution TEM (HRTEM) image (Fig. 2b) shows clear lattice fringes with interfringe distances of approximately 2.08 Å and 2.19 Å, suggesting that well-crystallized Mg-Al LDHs were formed.

To further evaluate the physical properties of Mg-Al LDHs including particle thickness and surface area, AFM, X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) measurements were performed. The thickness of Mg-Al LDHs was confirmed by tapping mode AFM (Fig. 2c and Fig. S4). It is shown that the Mg-Al LDHs particles located on a silicon wafer are flat, with a thickness of about 10 nm. The Mg-Al LDHs were characterized by powder-diffraction XRD (Fig. 2d). The result is entirely consistent with the standard pattern (JCPDS#89-0460), implying the formation of LDHs without any impurity phases. Meanwhile, the specific surface area derived from BET surface area measurements (Fig. S5) is 126 m2 g−1, with pore size predominantly located in 5 to 20 nm through desorption BJH pore plots; the pores result from the voids of Mg-Al LDH nanoparticles. These measurements, therefore, clearly demonstrate that as-prepared Mg-Al LDH nanoparticles are formed with a relatively uniform size and thickness, high surface area and good crystallization structure, all of which are favorable toward hydroxide ion conduction.

The Mg-Al LDH nanoparticles were then cold-pressed to form a membrane with a thickness of 900 μm to determine the hydroxide ion conductivity (Fig. S6). The conductivities tested at different relative humidities (RHs) and temperatures are presented in Fig. 3a. It is shown that the conductivity increases with an increase in temperature and RH, and the highest conductivity achieved at 80°C under RH=98% is 10.3 mS cm−1, which is slightly higher than the results reported elsewhere [28,33]. The superior conduction can be ascribed to: (1) the relatively uniform particle size and
the good crystallinity of Mg-Al LDHs, allowing the hydroxide ions to be conducted along the interlayers; (2) the absorbed water in Mg-Al LDHs. The influence of absorbed water on the conductivity can be proved by the increase in conductivity with the increased RH. Moreover, the conductivity of inorganic membrane shows an Arrhenius-type temperature dependence. The activation energies are 12.27 kJ mol\(^{-1}\) and 14.89 kJ mol\(^{-1}\) under RH = 98% and 80%, respectively. The result indicates that hydroxide ions are transported through the Grotthus mechanism, which is proposed as a possible way for hydroxide ion conduction [22], that is, hydroxide ions move through structural diffusion with the aid of carbonate anions located in the interlayer region. To validate the stability of the inorganic membrane, we continuously monitored the conductivity at 60 °C under RH = 98%. As shown in Fig. 3b, after the test for 200 hours, the inorganic membrane maintained its hydroxide conductivity of 7.7 mS cm\(^{-1}\), which is almost the same as the initial conductivity. The result suggests that the inorganic membrane has sufficient long-term stability for AEM water electrolysis. The excellent stability is attributed to the following reasons. For Mg-Al LDHs, the hydroxide ions are conducted through the interlayers with the assistance of the intercalated anions and absorbed water. The intercalated anions are not attacked by the hydroxide anions [21,35]. Additionally, it has been proven that the Mg-Al LDHs are thermally stable without the loss of interlayer water at the testing temperature (Fig. S7).

Further, we assembled the I\(^{-}\)MEA. The preparation process of I\(^{-}\)MEA is illustrated in Fig. S8. Characterization of the morphological structure of catalyst layers and the cross-section of I\(^{-}\)MEA were performed with SEM energy-dispersive X-Ray (EDX). Fig. 4a-b show representative SEM images of the anode electrode and the corresponding elemental maps of Cu and Mg, which respectively come from the Acta OER catalyst (CuCoO\(_x\), mixed oxides) [36] and Mg-Al LDHs. The even distribution of Cu and Mg elements on the entire detection area indicates that a uniform dispersion of

![Fig. 2](image_url)
Moreover, the interface between the catalyst layer and the anode and cathode, respectively. The i^MEAs and GDLs were carefully sandwiched by the titanium end plates. Several conditions which influence the performance of AEM water electrolysis were studied. Fig. 6a shows that the i^MEAs with a thick inorganic membrane caused a large overpotential due to the high internal resistance. Internal resistances of 3.27 Ω cm^2, 5.11 Ω cm^2, and 7.39 Ω cm^2 were respectively obtained in the i^ME system with membrane thicknesses of 300 μm, 500 μm, and 700 μm, despite the supply of 0.1 M NaOH in the anode channel. It should be noted that there is a trade-off between hydroxide ion conductivity and mechanical properties. A thin inorganic membrane increases the water electrolysis performance while reduces the mechanical strength, vice versa.

The performance of water electrolysis is also influenced by the electrolyte in the anode. In this work, we tested the performance of i^MEA system with various electrolytes: 0.1 M NaOH, 0.1 M Na2CO3, 0.1 M mixture (0.08 M Na2CO3+0.02 M NaHCO3), 0.1 M NaHCO3 and deionized (DI) water. Fig. 6b shows that the overpotential increases with a decrease in alkalinity. In particular, a large overpotential is induced when the pH is less than 10. We measured the internal resistance at 40 mA cm^-2 for this water electrolysis system using these electrolytes and the calculated results are listed in Table S1. These results suggest that the internal resistance is strongly determined by the pH of electrolyte. For example, the internal resistance increases from 3.27 Ω cm^2 to 8.39 Ω cm^2 when the pH is reduced from 12.63 to 8.51. An increase in internal resistance deteriorates the electrolysis performance. Meanwhile, the kinetics of oxygen evolution reaction becomes sluggish when the hydroxide ion concentration decreases, thereby causing a large overpotential. Nevertheless, it is demonstrated that the present i^MEA system is able to electrolyze water with weak alkaline solutions, even pure water.

As mentioned in Fig. 5e, the inorganic membrane can be thermally stable with a temperature as high as 120 °C. Thus, the effect of operating temperature on electrolysis performance was also studied. As shown in Fig. 6c, the cell efficiency can be significantly improved with an increase in operating temperature. The elevated temperature not only increases the ionic conductivity of Mg-Al LDHs, but also boosts the electrocatalytic activity of electrocatalysts. Our experiments showed that a maximum current density of 208 mA cm^-2 was achieved with a cutoff voltage of 2.2 V at 70 °C. At this current density, a large number of hydrogen gas bubbles was produced at the cathode. Although the performance was achieved at a high operating temperature and a relatively high voltage, the performance achieved here is still promising considering that the i^MEAs were fabricated with non-precious electrocatalysts and a thick inorganic membrane.

The long-term operating stability was studied for the i^MEAs through a continuous constant-current electrolysis. The i^MEA system was electrolyzed at a current density of 80 mA cm^-2 with two different aqueous solutions (0.1 M NaOH, 0.1 M Na2CO3). The long-term performances were studied at room temperature (25°C) and high temperature (60°C) with RH = 98%, respectively. The results are shown in Fig. 6a and 6b. It can be seen that the resistances of i^MEAs at both temperatures are relatively stable. The resistances of i^MEAs at 60°C are slightly higher than those at room temperature due to the higher operating temperature. The results of long-term performance are presented in Fig. 6c. It can be seen that the performances of i^MEAs at both temperatures are relatively stable. The performances of i^MEAs at 60°C are slightly higher than those at room temperature due to the higher operating temperature. The results of long-term performance are presented in Fig. 6c.
Fig. 4 SEM image (a) and EDS mapping (b) of the anode (OER), Cu and Mg respectively represent the Acta OER catalysts and Mg-Al LDHs. SEM image (c) and EDS mapping (d) of the cathode (HER), La and Mg respectively represent the Acta HER catalysts and Mg-Al LDHs. A low-resolution SEM image of cross-section (e) and EDS mapping (f), Co, Mg and Ni respectively represent the anode, inorganic membrane and the cathode respectively. (g) Elemental line-scanning profile of the integrated inorganic MEA along the green line shown in (h), Co, Ni, and Al are derived respectively from the anode, cathode, and membrane.
NaOH, 0.1 M Na₂CO₃) at 60 °C. As shown in Fig. 7, the cell voltage steadily increases from 1.881 V to 1.959 V with a decay rate of 130 μV h⁻¹ when the anode is fed with 0.1 M NaOH solution. Although the anode is fed with 0.1 M Na₂CO₃ solution, the cell voltage experiences a rapid increase during the initial 30 hours; the cell voltage subsequently increases from 2.038 V to 2.094 V with a decay rate of 100 μV h⁻¹. These results demonstrate that the cell voltage increases slightly during the entire testing process, exhibiting the superior stability of the system. The increase in the cell voltage is attributed, in part, to that of the carbonation of electrolyte during the course of electrolysis, and in part, to that of the degradation due to a scouring effect of electrolyte on the inorganic electrode [36]. The variation in the internal resistance of I²MEA was also measured during the electrolysis, revealing that the internal resistance stayed close to 3.33 Ω cm² and 4.42 Ω cm² when the anode was fed with 0.1 M NaOH and 0.1 M Na₂CO₃, respectively. The internal resistance was mainly caused by the thick inorganic membrane and the thick electrodes. The contact resistance between the catalyst layer and the inorganic membrane should be small due to the formation of the integrated structure. The superior stability of the I²MEA system is also demonstrated by virtually no change in system resistance during the course of constant-current electrolysis.

Finally, we compared the I²MEA water electrolysis with the alkaline water electrolysis and PEM electrolysis (Table S2). The voltage efficiency of the I²MEA water electrolysis is favorably comparable to that of the alkaline water electrolysis [37,38]. At present, however, the voltage efficiency of the I²MEA water electrolysis is still lower than that of the PEM water electrolysis due to the larger internal resistance. Although the application of the non-precious catalyst and Mg-Al LDHs reduces the capital cost of this system, the voltage efficiency should be further increased to reduce the operating cost as the electricity feedstock cost accounts for the main part of the total cost of hydrogen production [39,40]. To further increase the voltage efficiency, the approach to reduce the internal resistance needs be considered. For instance, the thickness of the catalyst layer and inorganic membrane can be reduced by fabricating the I²MEA

Fig. 5  Schematic of the home-made setup for alkaline water electrolysis. The insets show a digital photo of the setup and the circular single serpentine flow field.

Fig. 6  Polarization curves of AEM water electrolysis cell based on I²MEAs under various operating conditions: (a) membrane thickness; (b) electrolytes; (c) temperature. In panel (a) and panel (b), the cell temperature was fixed at 60 °C; the numbers in parentheses are internal resistances (Ω cm²) in panel (a) and pH value in panel (b). In panel (a) and (c), 0.1 M NaOH solution was employed as the electrolyte.
with a spin-coating method and this part of work is in progress in our group.

Conclusion

In summary, using a two-step approach, we synthesized Mg-Al LDHs, featured with uniform and thin hexagonal-platelet morphologies with a high surface area and well-crystallized structure. The Mg-Al LDHs with relatively high conductivity and good long-term stability are employed to fabricate novel integrated inorganic MEAs, in which Mg-Al LDHs play the role of the membrane and the solid electrolyte in the catalyst layers. Our experimental results demonstrate that the I2MEA system has a promising electrocatalytic activity and superior stability toward AEM water electrolysis owing to the integrated structure which allows hydroxide ions to transport smoothly. A maximum current density of 208 mA cm\(^{-2}\) is achieved with 0.1 M NaOH as the electrolyte and a cutoff voltage of 2.2 V at 70 °C. More significantly, the I2MEA system is electrolyzed with 0.1 M NaOH and 0.1 M Na\(_2\)CO\(_3\) for 600 hours with a relatively low degradation. Hence, our strategy of I2MEA fabrication is a simple synthesis preparation approach with a promising performance and durability toward water electrolysis. Most importantly, the approach demonstrated in the present work also offers a strategy for the fabrication of all-solid-state energy storage devices with solid electrolytes for a broad range of applications, including lithium ion batteries, supercapacitors, and solar cells.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2014.10.019.

Fig. 7 Long-term performance of AEM water electrolysis cells based on I2MEAs operating at a constant current density of 80 mA cm\(^{-2}\) at 60 °C with 0.1 M NaOH and 0.1 M Na\(_2\)CO\(_3\) as the electrolytes.

References

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