NANOMATERIALS

Single-layer nanosheets with exceptionally high and anisotropic hydroxyl ion conductivity

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When the dimensionality of layered materials is reduced to the physical limit, an ultimate two-dimensional (2D) anisotropy and/or confinement effect may bring about extraordinary physical and chemical properties. Layered double hydroxides (LDHs), bearing abundant hydroxyl groups covalently bonded within 2D host layers, have been proposed as inorganic anion conductors. However, typical hydroxyl ion conductivities for bulk or lamellar LDHs, generally up to $10^{-3}$ S cm$^{-1}$, are considered not high enough for practical applications. We show that single-layer LDH nanosheets exhibited exceptionally high in-plane conductivities approaching $10^{-1}$ S cm$^{-1}$, which were the highest among anion conductors and comparable to proton conductivities in commercial proton exchange membranes (for example, Nafion). The in-plane conductivities were four to five orders of magnitude higher than the cross-plane or cross-membrane values of restacked LDH nanosheets. This 2D superionic transport characteristic might have great promises in a variety of applications including alkaline fuel cells and water electrolysis.

INTRODUCTION

Two-dimensional (2D) materials are fundamentally and technologically intriguing because of the emergence of novel physical and chemical properties that are distinct from or absent in their bulk counterparts (1–5). This has been most markedly highlighted by the recent burgeoning research on semimetallic graphene (6–8), insulating hexagonal boron nitride (9), semiconducting black phosphorus (10–12), and transition metal dichalcogenides (13, 14), as well as versatile metal oxides such as titania and perovskite-type oxide nanosheets (15–18). The immense interest in 2D materials has been driven not only by the merit of preserving intrinsic properties of bulk layered hosts but also by the prospect of generating additional exotic characteristics arising from the ultimate anisotropy and/or confinement effects. This has led to rapid progress in using these 2D building blocks for a myriad of applications such as nanoelectronics, optoelectronics, flexible devices, catalysis, energy storage, and conversion.

Layered double hydroxides (LDHs) (19–21), with a general formula of $[\text{M}^{2+}\cdots\text{M}^{3+}\cdot(\text{OH})_{x}]^{z+}[\text{A}^{n-}\cdot\text{Hn}^{-}]^{z-}\cdot m\text{H}_{2}\text{O}$ (M represents metal cations, and A represents anions), are an important class of clay-like layered compounds consisting of alternately stacked positively charged host layers and weakly bound charge-balancing interlayer anions. The host layer consists of divalent/trivalent heterogeneous metal cations sandwiched between two hydroxyl slabs. The interlayer hydrated anions locate above/below the trivalent cationic charge centers to balance the positive host charge (22). A hydrogen bond network is thus developed among hydroxyl groups, interlayer anions, and water molecules in the gallery. LDHs are unique in the aspect that a vast majority of layered materials have negatively charged host layers and cations in the interlayer spaces. By appropriately adjusting anionic species, lamellar LDHs can be exfoliated into single-layer nanosheets, which may generate attractive properties arising from the ultimate 2D anisotropy and accessible high surface area, as well as a peculiar positively charged feature (23–30).

Recently, a few papers have reported the excellent proton-conducting properties of 2D-layered materials such as graphene oxide (GO) (31–34) and vermiculite (35). The results indicate that high proton conductivities could be achieved along 2D surfaces or reconstructed interlayer galleries. Bearing abundant hydroxyl groups covalently bonded within 2D host layers, LDHs belong to a relatively rare class of hydroxyl ion conductors. Several research groups have explored the prospect of using LDHs as inorganic solid electrolytes in alkaline fuel cells and water electrolysis (36–41). Current technology on fuel cells and electrolysis mostly involves an acidic environment that requires a dominant use of proton conductors/membranes, electrocatalysts based on precious metals, and anticrorosive electrodes. Despite the fact that precious metallic catalysts still dominate in achieving good performances in alkaline environment, a shift to alkaline operation environment using hydroxyl ion conductors, where nonprecious metallic catalysts can be used, may raise a feasibility of significantly reducing the cost. Unfortunately, a relatively lower ion mobility of OH$^{-}$ compared to H$^{+}$ limits the hydroxyl ion conductivity. Typical conductivities ($10^{-3}$ to $10^{-2}$ S cm$^{-1}$) for anion exchange membranes (AEMs) are not high enough compared to those for proton exchange membranes (PEMs), for example, Nafion ($\sim10^{-1}$ S cm$^{-1}$). In addition, commercial AEMs based on polymeric quaternary ammonium are usually associated with highly toxic preparation procedures, together with unsatisfactory thermal and chemical stability (42–44). These drawbacks have triggered the need of developing next-generation inorganic hydroxyl ion conductors. LDHs are highly regarded due to their reasonably high ionic conductivity, robust stability in alkaline environment, and resistance to carbonate degradation. However, only ion-conducting properties of bulk or lamellar LDH samples have been studied thus far. Intrinsic ionic conductivity of LDHs, particularly possible anisotropic transport behavior derived from an anisotropic bonding nature, is still unknown. The investigation on exfoliated LDH nanosheets will not only shed light on understanding the fundamental mechanism of hydroxyl ion conduction in LDHs but also have great implications in exploiting 2D building blocks for constructing novel architectures with superionic functions.

In the present work, we show that superior in-plane hydroxyl ion conductivities approaching $10^{-1}$ S cm$^{-1}$ could be achieved with LDH single-layer nanosheets, which were one to three orders of magnitude higher than the corresponding bulk precursors. A clear 2D anisotropy was attested by the poor cross-plane conductivities of restacked nanosheets, which were four to five orders of magnitude lower than the
in-plane values. In contrast, the conductivities of lamellar LDH platelets along the plate plane direction lay in the same order of magnitude as those of cold-pressed pellets containing randomly orientated platelets. These results clearly revealed an exceptionally high and anisotropic hydroxyl ion conduction of single-layer LDH nanosheets as a consequence of exposing the whole 2D surfaces. The exotic 2D-conducting properties might promise a great potential in a large array of energy- or environment-related applications.

RESULTS

Synthesis and characterization of LDH platelets and nanosheets, experimental setup, and determination of the conducting ionic species of LDH nanosheets

Well-crystallized, micrometer-sized, hexagon-shaped lamellar LDH platelets with various bimetallic host layer compositions [for example, Mg$^{2+}$-Al$^{3+}$, Co$^{2+}$-Al$^{3+}$, Co$^{2+}$-Co$^{3+}$, and Ni$^{2+}$-(Co$^{2+}$)-Co$^{3+}$] were synthesized according to the previously developed soft-chemical procedures (24–27). After exchanging the interlayer galleries for suitable anions, typically NO$_3^-$, LDH platelets were exfoliated in formamide for single-layer nanosheets. Detailed protocols and characterizations were provided in Materials and Methods and in figs. S1 to S3. The ion-conducting property of single-layer nanosheets was studied in comparison with the ion-conducting properties of parental LDH platelets and restacked nanosheets (Fig. 1A). As schematically illustrated in Fig. 1B, hydroxyl ions are supposed to be transported along adsorbed water molecules and hydroxide host layers through rapid hydrogen bond formation and cleavage, that is, a plausible Grotthuss mechanism (45). The ion conductivity was determined from AC impedance spectroscopic measurements on the LDH specimens at different temperatures and relative humidities (RHs) (31–33, 46). In particular, in-plane or 2D ion conductivity could be evaluated by depositing LDH nanosheets on comb-like microelectrodes (Fig. 1C and fig. S4).

The conducting ionic species of LDH nanosheets were determined by measuring the electromotive forces in a water vapor concentration cell by sending a humidified and dry O$_2$ gas stream on each side of a membrane (see the Supplementary Materials) (36). Electromotive forces were measured as open-circuit potentials or electrical voltages developed by charge separation across the membrane. The sign of electromotive forces determines the conducting ionic species, that is, a positive sign for cation conductors and vice versa. The electromotive forces of LDH (Mg-Al, Co-Al) nanosheet membranes were compared with commercial PEM (Nafion 117, DuPont) and AEM (AHA, ASTOM Co.), as well as GO membrane. As shown in Fig. 2, the same sign was observed for AEM (AHA) and LDH (Mg-Al, Co-Al) nanosheet membranes. GO membrane, which is already confirmed as a proton conductor (31), showed the same sign as PEM (Nafion). These results indicated that LDH nanosheets were conductors of negatively charged species. In addition, a huge sheet resistance ($10^7$ to $10^8$ ohms/square) was measured on LDH nanosheet membranes by a resistance meter (MCP-HT450, Mitsubishi Chemical Analytech). This was consistent with a recent study by Zhao et al. (47) on the electronic transport properties of 2D LDHs, demonstrating a hole conduction with a low carrier mobility. Therefore, a possible electronic conduction might be convincingly excluded, and LDH nanosheets were anion conductors.

Ionic conduction of LDH nanosheets

Single-layer Mg-Al LDH nanosheets with a lateral size of several micrometers and a thickness of ~0.8 nm (Fig. 3A) were deposited discretely on comb microelectrodes (Fig. 3, B and C). The resistance of bare comb electrodes was extremely high (on the order of 10$^8$ ohms; fig. S5), indicating that the coupling effect between adjacent comb teeth and the parasitic impedance contribution from bare electrodes was negligible. Typically, two types of nanosheets existed (Fig. 3B): (i) the bridging ones, connecting two opposite comb teeth, and (ii) the interior ones,

![Fig. 1. LDH and its hydroxyl ion conduction. Schematic diagrams for (A) the structure of LDH platelet, its exfoliation into single-layer nanosheets, and ion-conducting scenarios; (B) the plausible Grotthuss mechanism responsible for hydroxyl ion conduction; and (C) the measurement of in-plane ion conductivities of LDH nanosheets on comb electrodes.](http://advances.sciencemag.org/)
Fig. 2. Determination of conducting ion types. Electromotive forces of water vapor concentration cells using cation exchange membrane (Nafion 117, DuPont), AEM (AHA, ASTOM Co.), GO membrane, and Mg-Al (Co-Al) LDH nanosheet membranes as the electrolytes.

Fig. 3. Hydroxyl ion conduction of LDH nanosheets. (A) Atomic force microscopy (AFM) image of Mg-Al LDH nanosheets. Scanning electron microscopy (SEM) (B) and AFM (C) images of single-layer Mg-Al LDH nanosheets deposited on comb electrodes. (D) Representative Nyquist plots of impedance for single-layer Mg-Al LDH nanosheets on comb microelectrodes. The inset shows an enlarged view of the high-frequency section. (E) Temperature dependences of in-plane ionic conductivity for single-layer Mg-Al LDH nanosheets on comb microelectrodes. The inset shows an enlarged view of the high-frequency section.
interlayer gallery spacing as well as electrostatic repulsion from sandwiched and doubled interlayer anions.

With one representative sample of multilayer Mg-Al LDH nanosheets deposited on comb electrodes, the temperature dependences of in-plane ionic conductivity were measured during a large time interval of over half a year (fig. S9). The results show that the variations in ion conductivity could be neglected after such a long time, indicating that the as-exfoliated LDH nanosheets have excellent stability in terms of hydroxyl ion conduction. In addition, previous studies (52–54) on using exfoliated LDH nanosheets as electrode materials for fabricating supercapacitors showed that the charge-discharge performances of LDH-based supercapacitors did not undergo an obvious degradation even after several thousand cycles, indicating that LDH nanosheets have an excellent stability in strong alkaline environments (for example, 1 to 6 M KOH).

Cross-nanosheet or cross-plane hydroxyl ion–conducting properties were studied on lamellar membranes of restacked LDH nanosheets prepared by vacuum filtration (figs. S10 and S11). The cross-membrane conductivities increased with increasing temperature and RH, but the values for both Mg-Al and Co-Al LDH nanosheets were on the order of 10−6 S cm−1 even at 80% RH (fig. S11). Notably, the reducing the lateral dimension of LDH nanosheets from micrometers to several hundred nanometers yielded a proportional increase in cross-membrane conductivities, indicating that more interedge channels formed by reducing the lateral size of LDH nanosheets may be beneficial in contributing to cross-plane hydroxyl ion conduction.

Under a humidified environment, the adsorbed water molecules on LDHs underwent a self-dissociation process to generate protons and hydroxyl ions (55). This self-dissociation increased with temperature. Therefore, at elevated temperature, a higher concentration of hydroxyl ions (with an equal concentration of protons) would be generated. Because of the positive charges of LDH host layers, hydroxyl ions were attracted and propagated along the hydrogen bond networks of adsorbed water molecules and hydroxyl slab surface (nearest neighboring distance of OH−–OH centers, ~0.3 nm) through high-frequency hydrogen bond breaking and reformation. This led to the formation of a space-charge zone with an increased hydroxyl ion concentration around LDH host layers. The generated hydroxyl ions were rapidly conducted, which broke the water self-dissociation equilibrium, leading to the sustaining generation of sufficient flow of hydroxyl ions. Through an isotope effect experiment (fig. S12) in which the ionic conductivities of representative LDH nanosheet samples were measured in H2O and D2O atmospheres in both real-time and static states, hydroxyl ions, rather than protons, could be verified to be the vehicle of ion conduction from the negligible variations in ionic conductivities upon replacing the atmosphere from H2O to D2O. For LDH nanosheets, the charge-balancing anions were distributed on both surfaces. The hydroxyl ion conduction was confined on the 2D slab surfaces without serious restraint from adjacent layers (because of the larger interlayer spacing of single- and multilayer assemblies, as compared in figs. S2 and S13). Electrostatic repulsion from the interlayer hydrated anions might also be relieved to some extent because of the presence of abundant spacing for hydroxyl ions to choose their conduction pathways. Hydroxyl ions might propagate through the fully hydrated covalently bonded hydroxide surfaces following the Grotthuss mechanism (45), that is, rapid hydrogen bond formation/cleavage with the aid of adsorbed water (Fig. 1B), yielding extremely high in-plane ion conductivities (Fig. 3 and figs. S7 to S9). However, the propagation may be slowed down in limited interlayer galleries of crowded anions, leading to decreased conductivities for lamellar platelets. In addition, the cross-plane

![Fig. 4. Hydroxyl ion conduction of LDH platelets.](http://advances.sciencemag.org/)

**Fig. 4. Hydroxyl ion conduction of LDH platelets.** SEM images of (A) Co-Al-CO3<sup>2−</sup> and (B) Co-Ni-Br<sup>−</sup> LDH hexagonal platelets deposited on comb electrodes. The inset in (A) shows an AFM image of isolated Co-Al-CO3<sup>2−</sup> LDH platelet on comb teeth. (C) Representative Nyquist plots of impedance for Co-Ni-Br<sup>−</sup> LDH platelets on comb electrodes. The inset shows an enlarged view of the high-frequency section. (D) Temperature dependences of ionic conductivity for various kinds of LDH platelets at 80% RH.
hydroxyl ion conduction should rely on interlayer hopping, which may be severely impeded by the interlayer anions and a large gallery spacing (~1 nm) (fig. S13), resulting in much slower transport than the in-plane case.

**Ionic conduction of lamellar LDH platelets**

To distinguish the ion transport behavior of single-layer nanosheets from lamellar platelets, we evaluated the hydroxyl ion conductivity of LDH platelets with the assistance of comb electrodes. Through an oil/water interfacial self-assembling procedure by Ma et al. (56), closely packed films of LDH platelets with a typical thickness of several tens of nanometers and a lateral dimension of several micrometers were assembled on comb electrodes. Figure 4 (A and B) shows SEM and AFM characterizations of the representative packing of LDH hexagonal platelets. Figure 4C depicts the representative variations of impedance of LDH platelet samples containing randomly orientated LDH platelets. This could be attributed to the bulk nature of LDH platelets in both cases, which reflected the overall conduction characteristics, in stark contrast to the ultimate 2D anisotropic feature of single-layer nanosheets.

As control experiments, lamellar LDH platelets were cold-pressed into pellets. Within the pellets, LDH platelets were randomly oriented to the specimen surface. The measured conductivities, which also increased with temperature and RH (figs. S14 and S15), thus reflected bulk and average characteristics of LDH compounds. As shown in fig. S15, there was a significant enhancement in ion conductivities after anion exchange from CO$_3^{2-}$ to monovalent (Cl$^-$, Br$^-$, and NO$_3^-$) forms. Compared to CO$_3^{2-}$ LDHs (10$^{-6}$ to 10$^{-4}$ S cm$^{-1}$), the conductivities of Cl$^-$/Br$^-$ and NO$_3^-$ LDHs increased to the order of 10$^{-4}$ and 10$^{-3}$ S cm$^{-1}$, respectively. Accordingly, the activation energy $E$ values decreased in the same order. The change tendencies of ion conductivity and related $E$ value with respect to interlayer anionic species resonated well with the variation of gallery spacing (fig. S2), indicating that the increase in the interlayer spacing of LDHs might favor hydroxyl ion conduction in host layers. Notably, the measured conductivities of LDH platelets assembled on comb electrodes were close to those of pellet samples. This could be attributed to the bulk nature of LDH platelets, reflecting the overall conduction characteristics.

**Summary and comparison of ionic conductivities for LDH nanosheets and lamellar platelets**

Typical hydroxyl ion conductivities of LDH nanosheets and hexagonal lamellar platelets are compared and summarized in Fig. 5. All the in-plane conductivities of Mg-Al and Co-Al LDH nanosheets were extremely high, which were on the order of 10$^{-2}$ S cm$^{-1}$ and approaching 10$^{-1}$ S cm$^{-1}$ for single-layer sheets, whereas the cross-plane values were ultralow, which were only on the order of 10$^{-6}$ S cm$^{-1}$. The highly
anisotropic hydroxyl ion conductivities were attributed to the morphological and structural anisotropy originating from the exfoliation of LDH crystals to ultimate 2D nanosheets. By contrast, pellet samples containing randomly orientated LDH platelets yielded values in the same order of magnitude as the platelets measured along the plate plane direction on comb electrodes. In general, the conductivities of unexfoliated LDHs were one to three orders of magnitude lower than the in-plane values of LDH nanosheets, demonstrating the possibility of exploiting the 2D full-exposure effects arising from dimensionality reduction for superior ion/mass transport properties. This highly anisotropic ion-conducting characteristic of LDH nanosheets should be taken into full account for fabricating hydroxyl ion conductors or AEMs, that is, the ultrahigh in-plane conduction should be maximized, whereas the ultralow cross-plane transport should be minimized. Here, we propose two possible routes: One might be to perpendicularly align and immobilize LDH nanosheets in a matrix to create ultrafast ion conduction pathways along nanosheet planes, similar to the reports on anisotropic hydrogels of cofacially aligned oxides nanosheets (57, 58); the other might be to first assemble LDH nanosheets into large-area lamellar membranes (fig. S10), then scroll into Archimedean spiral fibers, similar to the preparation of layered and scolled graphene-based nanocomposites (59), and finally cut along the direction perpendicular to the axis of the fiber to produce thin membranes with spiral ultrafast in-plane conduction pathways. Taking in consideration that various liquid-phase membrane formation techniques (for example, drop casting, vacuum filtration, and spin coating) are available, such technological innovations could enable the promises of LDH nanosheets as an inorganic anion exchange conductor for practical electrochemical devices.

**DISCUSSION**

In summary, we have demonstrated that the in-plane hydroxyl ion conductivities of single-layer LDH nanosheets, approaching $10^{-3}$ S cm$^{-1}$, were four to five orders of magnitude higher than those of crossplane transport and one to three orders of magnitude higher than the measured values of corresponding bulk LDH precursors. The current study has unveiled the 2D confinement-induced highly anisotropic hydroxyl ion conduction in LDH nanosheets, which may be considered an intrinsic characteristic of this peculiar 2D material. The superionic conductivity of LDH nanosheets may endow them with great potential, albeit technological innovations are needed, for high-performance hydroxyl ion conductors and AEMs useful in electrochemical energy storage and conversion, catalysis, sensing, and chemical filters.

**MATERIALS AND METHODS**

**Preparation of LDH platelets and nanosheets**

LDH platelet samples were synthesized using hexamethylenetetramine (HMT) $\cdot$ C$_6$H$_{12}$N$_4$ hydrolysis of a mixed solution of Mg(NO$_3$)$_2$·6H$_2$O and Al(NO$_3$)$_3$·9H$_2$O (Mg/Al ratio of 2) under hydrothermal treatment (24). For comparison, commercial samples of Mg$_{0.5}$Al$_{0.5}$CO$_3$$^{2-}$ LDHs were also used, which were synthesized by coprecipitation of Mg(NO$_3$)$_2$·6H$_2$O and Al(NO$_3$)$_3$·9H$_2$O mixed solution (Mg/Al ratio of 3) in the presence of Na$_2$CO$_3$. Co$_{0.25}$Al$_{0.75}$CO$_3$$^{2-}$ LDH hexagonal platelets were synthesized from a mixed solution of CoCl$_2$·6H$_2$O and AlCl$_3$·9H$_2$O using urea [CO(NH$_2$)$_2$] as a hydrolysis agent (25).

Co$_{2/3}$-Co$_{2/3}$-Br$^-$ and Co$_{2/3}$-Br$^-$ LDH hexagonal platelets were synthesized on the basis of a topchemical oxidative intercalation technique by Ma et al. (26) and Liang et al. (27). In this procedure, brucite-like β-Co(OH)$_2$ and Co$_{0.25}$Ni$_{0.75}$0(OH)$_2$ hexagonal platelets were first synthesized via HMT hydrolysis of CoCl$_2$·6H$_2$O solution and CoCl$_2$·6H$_2$O/NiCl$_2$·6H$_2$O mixed solution (Co/Ni ratio of 2), respectively. Subsequently, they were transformed into Co$_{2/3}$-Co$_{2/3}$-Br$^-$ and Co$_{0.25}$Ni$_{0.75}$-Br$^-$ LDHs through partial oxidation of Co$^{2+}$ into Co$^{3+}$ with Br$_2$/CH$_3$CN. Simultaneously, Br$_2$ itself was reduced to Br$^-$. Interlayer exchange of LDH host layers.

Anion exchange was performed via a salt-acid treatment (24–27). Briefly, by treating Mg$_{2/3}$-Co$_{1/3}$CO$_3$$^{2-}$ and Co$_{2/3}$-Al$_{1/3}$CO$_3$$^{2-}$ LDH hexagonal platelets in a salt-acid mixed solution (for example, NaCl-HCl, NaN$_3$-HNO$_3$, and NaBr-HBr), CO$_3$$^{2-}$ LDHs could be exchanged into Cl$^-$, NO$_3^-$, and Br$^-$ forms, respectively. By dispersing Co$_{2/3}$-Co$_{2/3}$-Br$^-$ and Co$_{0.25}$Ni$_{0.75}$-Br$^-$ LDH hexagonal platelets in a Na$_2$CO$_3$ solution, they could be converted into CO$_3$$^{2-}$ forms.

Mg$_{2/3}$-Al$_{1/3}$NO$_3^-$ and Co$_{2/3}$-Al$_{1/3}$NO$_3^-$ LDH hexagonal platelets were chosen for exfoliation to yield single-layer nanosheets. The samples (100 mg) were dispersed in (200 ml) formamide (HCONH$_2$). Treating the suspensions with mechanical shaking for 2 days could yield single-layer LDH nanosheets with typical lateral dimensions of several micrometers. Sonication for 3 hours resulted in nanosheets with reduced lateral sizes to several hundred nanometers.

**Deposition of LDH nanosheets and platelets on comb microelectrodes**

The deposition of LDH nanosheets on comb electrodes was performed using a drop-casting method previously proposed (31–33). For discrete single-layer nanosheet assembly, a droplet (0.5 μl) of dilute LDH nanosheet suspension (0.05 mg/ml) was drop-casted onto comb electrodes, followed by quickly swabbing the droplet away and drying the electrodes at 60°C for 12 hours.

An oil/water interfacial self-assembling procedure was used for the deposition of closely packed films of LDH platelets on comb electrodes (56). Co$_{0.25}$Al$_{0.75}$CO$_3$$^{2-}$, Co$_{2/3}$Al$_{1/3}$NO$_3^-$, and Co$_{2/3}$Ni$_{0.75}$-Br$^-$ LDH hexagonal platelets (100 mg) were uniformly dispersed in 50 ml of water under sonication. Subsequently, hexane (4 ml) was added to form a hexane/water interface, followed by dropwise addition of isopropanol (2 ml). After most hexane was evaporated, a continuous film floating on the interface was visible, which was transferred onto comb electrodes using the vertical lifting method, followed by drying at 60°C for 12 hours.

**Preparation of lamellar membranes of LDH nanosheets**

A vacuum-assisted filtration method was used to prepare lamellar membranes. Briefly, 30 ml of Mg-Al (Co-Al) LDH nanosheet formamide suspension (0.5 mg/ml) was vacuum-filtered through a piece of polyvinylidene difluoride microfilter (pore diameter, ~0.2 μm; porosity, ~80%), followed by drying at 60°C for 12 hours. Consequently, the LDH nanosheet membrane could be easily detached from the microfilter for freestanding operation. Both membrane surfaces were evaporated with Pt (6 mm in diameter), followed by attaching to silver wires with silver paste as the electrodes for cross-plane ionic conductivity measurements.

**Preparation of LDH platelet-based pellets**

LDH platelet samples were cold-pressed into disc-shaped pellets under a pressure of ~500 MPa. The diameter and thickness of the pellets...
were 7 and <0.5 mm, respectively, which could be precisely measured by SEM observations. Both surfaces of the pellets were evaporated with Pt (6 mm in diameter). Bulk ionic conductivities of LDH platelets were assessed on these sandwiched Pt/pellet/Pt specimens.

Measurement of ionic conductivity

Ionic conductivities were determined from AC impedance spectra measured with an LCR meter (6500P, Wayne Kerr) in a frequency range from 20 Hz to 10 MHz in a constant temperature and humidity chamber (IVV 223, Yamato Scientific Co. Ltd.). The impedance data were then transferred to the ZIPlot/ZView software package (Scribner Associates). Nyquist plots usually displayed a compressed semicircle in the high-frequency range and an inclined straight line in the low-frequency range. The low-frequency end of the semicircle and the high-frequency end of the straight line generally coincided and represented the bulk resistance ($R$) (46). In plots where the semicircles were not well discerned, the interception of the high-frequency tail of the straight line with the real axis was extracted as the resistance, which was cross-checked by equivalent circuit analysis (46). The details of the calculation of ionic conductivity ($\sigma$) from measured values of resistance $R$ were provided in the Supplementary Materials.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/4/e1602629/DC1

**REFERENCE AND NOTES**


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