Genuine divalent magnesium-ion storage and fast diffusion kinetics in metal oxides at room temperature

Jinlin Yang, Jibiao Li, Wenbin Gong, and Fengxia Geng

Rechargeable multivalent metal-ion batteries are promising energy sources that can potentially satisfy the existing demand for high-energy density electrochemical energy storage devices. The electrochemical discharge and charge reactions in these batteries involve multiple electron transfers per ion, which may significantly increase the ion storage capacity relative to that of monovalent batteries. Among the studied systems, Mg-ion batteries utilizing divalent magnesium ions (Mg2+) as charge carriers are considered the most viable option. In addition to their numerous advantages such as abundant Mg resources, low fabrication cost, and environmental friendliness, these batteries exhibit dendrite-free Mg plating and stripping during electrochemical cycling, which ensure high operational safety. Furthermore, the volumetric capacity of Mg anodes (3,833 mAh · cm⁻³) is almost twice as large as that of Li anodes (2,062 mAh · cm⁻³) (3–5). Unfortunately, it is very difficult to realize genuine storage and fast transport of Mg2+ ions in solids (especially in inorganic oxides) at low temperatures due to their high degree of polarization and charge density. The charge of the Mg2+ ion is two times larger than that of the Li+ ion, although the ionic radius of Mg2+ (0.72 Å) is close to that of Li+ (0.76 Å). As a result, Mg2+ ions are more likely to form strong covalent bonds with electrolytes (such as Mg–Cl bonds in the commonly used all-phenyl complex electrolytes) with very high dissociation energy. Meanwhile, the strong electrostatic interactions between Mg2+ ions and solid host lattices significantly inhibit their diffusion kinetics in these lattices. Resultantly, the migration barrier for Mg2+ ions is usually higher than that for Li+ ions in the same cathode material (6–8).

To overcome the Mg bond dissociation barrier and enhance Mg-ion diffusion kinetics, intercalation chemistries based on solvated Mg2+ as the intercalating cation species, including Mg(DME)3+, Mg(H2O)2+, and MgCl+, have been established (9–11). These complex ions lower the charge density by either increasing the ionic radius or decreasing the net charge. Although the storage of these complex ions alleviates the drawbacks related to the dissociation and diffusion of bare Mg2+ ions, it produces several challenges. The practical energy densities at the cell level for the hybrid battery based on such intercalation chemistry are lower than that of the battery exclusively involving Mg2+ storage. Additionally, the coinsertion of these bulky solvent molecules induces significant volume changes of the electrode, thereby limiting its cycle life. Recently, a two-pronged approach has been developed to overcome these challenges (12). It involved the storage of exclusively Mg2+ ions and their fast solid-state diffusion in an organic cathode fabricated from pyrene-4,5,9,10-tetraone. Heterogeneous enolization redox chemistry was utilized to avoid the bond cleavage and reformation; meanwhile, an electrolyte comprising weak-coordinated anions in an ethereal solvent blend was employed to increase the bulk ion mobility and promote Mg2+ desolvation on the electrode surface. However, it still remains a critical challenge in inorganic materials to overcome the two important problems: the ion dissociation in the conventional Mg chloride complex electrolyte and solid-state ion diffusion.

The development of rechargeable inorganic cathodes for Mg batteries using a rational structural design is the major limiting factor of this promising post–Li-ion battery technology. Metal oxides are the most promising electrode materials for Li-ion batteries, taking advantage of their excellent chemical and thermal stabilities; however, this is not always true for Mg-ion batteries. Compared to sulfides and selenides, most metal oxides suffer from low reversible capacities and slow diffusion kinetics, owing to the higher strength of the Mg–O bond as compared to lithium-ion technology that can potentially overcome its safety, cost, and energy density limitations. Nevertheless, the development of a competitive room temperature magnesium battery has been hindered by the sluggish dissociation of electrolyte complexes and the low mobility of Mg2+ ions in solids, especially in metal oxides that are generally used in lithium-ion batteries. Herein, we introduce a generic proton-assisted method for the dissociation of the strong Mg–Cl bond to enable genuine Mg2+ intercalation into an oxide host lattice; meanwhile, the anisotropic Smoluchowski effect produced by titanium oxide lattices results in unusually fast Mg2+ diffusion kinetics along the atomic trough direction with a record high ion conductivity of 1.8 × 10⁻⁴ S · cm⁻¹ on the same order as polymer electrolyte. The realization of genuine Mg2+ storage and fast diffusion kinetics enabled a rare high-power Mg-intercalation battery with inorganic oxides. The success of this work provides important information on engineering surface and interlayer chemistries of layered materials to tackle the sluggish intercalation kinetics of multivalent ions.

Mg-ion intercalation chemistry | two-dimensional sheets | metal oxides

Rechargeable magnesium batteries represent a viable alternative to lithium-ion technology that can potentially overcome its safety, cost, and energy density limitations. Nevertheless, the development of a competitive room temperature magnesium battery has been hindered by the sluggish dissociation of electrolyte complexes and the low mobility of Mg2+ ions in solids, especially in metal oxides that are generally used in lithium-ion batteries. Herein, we introduce a generic proton-assisted method for the dissociation of the strong Mg–Cl bond to enable genuine Mg2+ intercalation into an oxide host lattice; meanwhile, the anisotropic Smoluchowski effect produced by titanium oxide lattices results in unusually fast Mg2+ diffusion kinetics along the atomic trough direction with a record high ion conductivity of 1.8 × 10⁻⁴ S · cm⁻¹ on the same order as polymer electrolyte. The realization of genuine Mg2+ storage and fast diffusion kinetics enabled a rare high-power Mg-intercalation battery with inorganic oxides. The success of this work provides important information on engineering surface and interlayer chemistries of layered materials to tackle the sluggish intercalation kinetics of multivalent ions.

Significance

Rechargeable Mg batteries constitute safe and sustainable high-energy density electrochemical energy storage devices. However, due to an extremely high charge density of Mg2+ ions, “real” Mg2+-intercalation chemistry has been rarely realized, and significantly accelerated Mg2+-diffusion kinetics is always encountered, especially in metal-oxide systems. Herein, we demonstrate a generic strategy to overcome the hitherto insurmountable challenge of developing rechargeable metal-oxide electrode materials for Mg batteries, with genuine Mg2+ storage, record fast diffusion kinetics, and excellent cycling performance.

Author contributions: F.G. designed research; J.Y. performed experimental research; J.L. and W.G. conducted simulation; and J.Y. and F.G. analyzed data and wrote the paper. The authors declare no competing interest.

This article is a PNAS Direct Submission. This open access article is distributed under Creative Commons Attribution License 4.0 (CC BY).

1To whom correspondence may be addressed. Email: gengfx@suda.edu.cn.

This article contains supporting information online at https://www.pnas.org/lookup/suppl/doi:10.1073/pnas.2111549118/-/DCSupplemental.

Published September 14, 2021.
with those of the Mg–S and Mg–Se bonds (7, 13). Furthermore, the reaction of Mg ions with highly polarizable O²⁻ ions often leads to MgO formation rather than Mg²⁺ intercalation, making it almost impossible to achieve reversibility in oxide-based cathodes (14). Therefore, the development of rechargeable metal-oxide electrode materials for Mg-ion batteries characterized by genuine Mg²⁺ storage, fast solid-state diffusion kinetics, and excellent cycling performance (especially at room and low temperatures) remained an unsurmountable challenge.

In the present study, genuine Mg²⁺ intercalation/deintercalation and fast diffusion in oxide lattices were realized not only at room temperature but also at subzero temperatures. These outstanding results were achieved by placing protons on negatively charged metal-deficient oxide sheets and disorderly stacking these sheets over a certain distance (this strategy is schematically illustrated in Fig. 1). The stripping of Cl⁻ ions was facilitated by the presence of protons between the sheets, while fast Mg²⁺ diffusion was ensured by the extension of the wavefunction along an atomic trough on the unique sheet surface due to the anisotropic Smoluchowski effect. This induced the formation of flat potential-energy surfaces and diffusion highways, which gave a record high Mg-ion conductivity of 1.8 × 10⁻² S cm⁻¹. As a result, the fabricated Mg-ion cell exhibited a high-power density of 7.4 kW kg⁻¹ while maintaining an energy of 113.0 Wh kg⁻¹. Practically, the cell battery, which was charged at room temperature and almost impossible to achieve reversibility in oxide-based cathodes, remained an unsurmountable challenge. Therefore, the development of rechargeable metal-oxide electrode materials for Mg-ion batteries characterized by genuine Mg²⁺ storage, fast solid-state diffusion kinetics, and excellent cycling performance (especially at room and low temperatures) remained an unsurmountable challenge.

Results and Discussion

Titanium oxide sheets with a net negative charge (Ti₁.₇₄O₄₁.₀₄⁻) were selected for a representative study. These sheets were obtained via soft chemical delamination using layered K₆₋₃Ti₁.₇₃Li₀.₂₇O₄ as a precursor, being protonated in acid and delaminated in tetramethylammonium hydroxide (SI Appendix, Fig. S1) (15). A certain number of protons and electrolyte traces remained as residues on the sheet surfaces. The protons could be in the form of hydronium ions or hydroxyl being adsorbed on oxygen atoms at the vertexes of the TiO₆ octahedra. The atomic force microscopy images revealed that the synthesized titanium oxide sheets had lateral sizes of 2 to 6 μm and thicknesses of 1.1 nm (Fig. 2A). The thickness value was consistent with the sum of the crystallographic parameters determined for a single titanium oxide layer (0.75 nm) and the adsorbed ions (16, 17). The Ti₁.₇₄O₄₁.₀₄⁻ sheets exhibited a high density of net negative charges (9.12 nm⁻²), which enabled electrostatic self-assembly with the positively charged guests such as protonated amines (SI Appendix, Fig. S2). A series of primary amines with various alkylation lengths were investigated to determine the states of guest amines in the galleries. The presence of two X-ray diffraction (XRD) peaks corresponding to the (200) and (002) intrasheet reflections indicated that the structure of elementary lepidocrocite sheets was maintained throughout the entire process (Fig. 2B and SI Appendix, Fig. S3). An analysis on the interlayer gap-dependent (00l) stacking reflections along with density functional theory (DFT) calculations revealed that alkyl chains were likely arranged in a bilayer, paraffin-like conformation, which is a typical structure of layered materials (SI Appendix, Figs. S3 and S4) (18). The tilting angle was ~30°. The absence of general (hkl) reflections indicated a disordered stacking of the sheets and the absence of a registry between the neighboring sheets. The sheets protonated with the amines also showed step increment in thickness, confirming the interaction of the ammonium ions with the negatively charged titanium oxide sheets (SI Appendix, Fig. S5). The hexylammonium-spaced specimen was selected for further detailed studies owing to its optimal electrochemical properties. The hexylammonium-spaced specimens were described by the formula (Ti₁.₇₄O₄)₁.₀₄⁻·[(C₆H₁₆N)+·0.₉₀(H³⁺)₀.₆₅·1.₃H₂O] (SI Appendix, Fig. S6), containing one amine group for every 2.77 unit cells of titanium oxide. The results of scanning electron microscopy observations revealed that the obtained specimen exhibited a platelet-like morphology with a lateral size of 2 to 10 μm and thickness of 10 to 20 nm (Fig. 2C and SI Appendix, Fig. S7). From the interlayer spacing of 1.77 nm estimated by XRD, it was found that each platelet comprised a stack of 17 sheets. Cross-sectional high-resolution transmission electron microscopy (HR-TEM) images indicated the presence of a stacking structure with an interlayer distance of 1.7 nm (SI Appendix, Fig. S8), which was in good agreement with the XRD data. The Fourier-transform infrared spectroscopy (FTIR) and Raman spectra confirmed the hybridization of the titanium oxide phase with protonated alkylamines (SI Appendix, Fig. S9). As the dissociation energy of the Mg–Cl bond was significantly lowered in the presence of protons (vide post, see Fig. 5E and related explanations), the ability of the oxide structure to generate protons (Brønsted acidity) was evaluated by studying the adsorption of weakly basic pyridine probe, assuming that this process could occur only at highly acidic sites. The dominant IR bands located at 1,488 and 1,540 cm⁻¹ in Fig. 2D are characteristic of pyridinium ions (protonated pyridine), indicating a high Brønsted acidity, which likely originated from the presence of protons between the layers (19). The obtained results revealed that the analyzed structure comprised a disordered lamellar stack of titanium oxide sheets with tilled alkylamines and protons in the galleries.

The electrochemical activity of the designed oxide electrode for Mg-ion storage was evaluated using a coin cell with an Mg

![Fig. 1](https://doi.org/10.1073/pnas.2111549118)

Genuine divalent magnesium-ion storage and fast diffusion kinetics in metal oxides at room temperature
anode. A standard all-phenyl Mg chloride complex electrolyte (0.4 M 2PhMgCl-AlCl₃ in tetrahydrofuran) was utilized due to its high Coulombic efficiency for the reversible deposition of Mg (SI Appendix, Fig. S10). The estimated theoretical capacity based on complete reduction of Ti⁴⁺ to Ti⁰ was ∼317 mAh · g⁻¹ (1.73 charges per formula unit). Fig. 3A displays the charge–discharge profiles recorded at a low current rate of 0.05 A · g⁻¹ after an activation cycle (SI Appendix, Fig. S11). Although divalent Mg ions generally exhibit low mobility, and a relatively high temperature is required to achieve a satisfactory battery capacity, a discharge capacity of 260 mAh · g⁻¹ was obtained at a practical current density of 50 mA · g⁻¹ (0.16 C) and room temperature (25 °C). The obtained discharge capacity corresponded to 1.42 electron transfers per formula unit (82% of the theoretical value). The results of inductively coupled plasma–atomic emission spectroscopy measurements revealed that the Mg content in the studied sample was 0.76 (SI Appendix, Fig. S12). The compositions of intercalated species were then determined from the charge and Mg content; surprisingly, the main intercalated included divalent Mg²⁺ and MgCl⁺ ions with a molar ratio of 0.66:0.10. A quantitative analysis by energy-dispersive X-ray spectroscopy produced consistent results with a C₆H₁₆N, MgCl⁺ and H₂O components in the fully discharged and charged electrodes were equal to 1:0.76:0.09:1.1 and 1:0.07:0.09:1.1, respectively (SI Appendix, Fig. S13). The content of hexaammonium cations remained unchanged, which helped maintain the stacking structure. Furthermore, the lattice water was retained in the lattice without penetrating the electrolyte. The effect of temperature on the cell performance was investigated as well. At an operating temperature of 55 °C, the cell exhibited a high capacity of 312 mAh · g⁻¹ (1.73 charges per formula unit), which was close to the theoretical value. More impressively, high-capacity retention was observed at low operating temperatures (Fig. 3A), revealing that 55% of the cell capacity at a room temperature of 25 °C was retained at a subzero temperature of −15 °C. The capacity retention properties of the fabricated electrode at a subzero temperature were superior to those reported previously for TiS₂ (28%) (11) and VS₄ (15%) (22) electrodes.

The high charge density of divalent Mg cations generally result in slow solid-state diffusion (especially in metal-oxide lattices), which significantly lowers the power output of Mg batteries. The diffusion coefficient of the system developed in the present study was estimated using a galvanostatic intermitent titration technique. The Mg²⁺ diffusion decreased from 2.1 × 10⁻⁸ to 1.5 × 10⁻¹⁰ cm² · s⁻¹, with an increase in the Mg²⁺ concentration in the host lattice (Fig. 4D). This decrease was likely caused by electrostatic repulsion; however, the observed range of the Mg²⁺ diffusion coefficient indicated relatively fast charge transfer kinetics. Its values obtained for the designed experimental system were ∼10⁻⁹ to 10⁻¹¹ higher than those of previously reported Mg²⁺-intercalation materials (23–26), including cubic thiospinel Ti₂S₃ and Chevrel phase Mo₅S₈ (∼10⁻¹⁰ to 10⁻¹² cm² · s⁻¹) and even comparable with MgCl⁺ and Li⁺ diffusivity (∼10⁻⁹ cm² · s⁻¹) (11, 22, 27–31), as summarized in
Genuine divalent magnesium-ion storage and fast diffusion kinetics in metal oxides at room temperature

Fig. 3. Genuine Mg$^{2+}$ (de)intercalation in the oxide electrode. (A) Voltage-capacity profiles obtained for the Mg$_2$Ti$_{1.74}$O$_4$ electrode at temperatures between $-15$ and $55$ °C. The values of $x$ were estimated via inductively coupled plasma elemental analysis. TOF-SIMS profiles recorded for the (B) positive Mg ions and (C) Cl-containing ions emitted from the discharged electrode. The secondary ions (i.e., Mg$^+$ and Cl$^-$) were generated via the interactions with the Bi$^{+}$ beam used for analysis. (D) TOF-SIMS depth profiles of various chemical species present in the discharged electrode. The specimen depth was calculated based on the calibrated Cs$^+$-sputtering rate of $\sim 0.03$ nm s$^{-1}$. (E) $^{25}$Mg NMR spectrum of the discharged electrode.

Fig. 4B. Strikingly, as the temperature dropped to $-15$ °C, the Mg$^{2+}$ diffusion coefficient remained in the range of $10^{-9}$ to $10^{-11}$ cm$^2$·s$^{-1}$, validating the rapid ion diffusion in the studied system. The ion conductivity was also examined with typical impedance spectroscopy measurements, which gave a value of $1.8 \times 10^{-4}$ S·cm$^{-1}$ at room temperature (SI Appendix, Fig. S14), although a high temperature of $>500$ °C is typically essential for enabling Mg$^{2+}$ transportation. The contributions from both electronic conductivity and motion of protons were negligible (SI Appendix, Fig. S15). Comparing with all reports as far as we know, this is still the highest record, even magnitudes higher than excellent ion-conducting metal–organic framework materials (SI Appendix, Table S1).

The fast diffusion kinetics in the prepared titanium oxide electrodes resulted in stable and high-rate capability, even in the case of thick electrodes with mass loadings ranging from 1 to 5 mg·cm$^{-2}$ (Fig. 4C). At a typical loading amount used in research studies (1 mg·cm$^{-2}$), the electrode exhibited good capacity retention varying from 260 to 241, 221, 198, 178, 156, 135, 118, and 100 mA·h·g$^{-1}$ as the current density progressively increased from 50 to 100, 200, 500, 1,000, 2,000, 3,000, and 4,000, and 5,000 mA·h·g$^{-1}$ (16 C), respectively. Even at a high mass loading of 5 mg·cm$^{-2}$, the discharge capacity reached a high value of 240 mA·h·g$^{-1}$ at a current density of 50 mA·g$^{-1}$ operated in lean electrolyte conditions (7.6 µL·mg$^{-1}$), illustrating the feasibility of fabricating high-mass loading electrodes with high energy and power performance. The obtained maximum power density was 7.4 kW·kg$^{-1}$ while maintaining an energy of 113.0 Wh·kg$^{-1}$, which was the highest value ever reported for inorganic Mg$^{2+}$ and MgCl$^+$ storage systems (SI Appendix, Table S2). Practically, the cell that was rapidly charged at 15 A·g$^{-1}$ (47 C) in 55 s could stably run for over 4.5 h at a current of 0.05 A·g$^{-1}$ (0.16 C) (SI Appendix, Fig. S16). This is quite appealing for many real-world applications, such as smartphones obtaining an adequate battery life by recharge within 1 min.

The electronegative O atoms in the host lattices of typical oxides tend to trap Mg$^{2+}$ ions, which prevents their release during charging reactions, resulting in the occurrence of irreversible reactions and poor cycling performance (6, 32). Impressively, the oxide electrode developed in this study demonstrated excellent long-term stability. At a current density of 500 mA·g$^{-1}$ (1.6 C) and extended run over 2,000 cycles, the capacity retention was 81% with a decay rate of 0.0095% per cycle (Fig. 4D). When the operating temperature decreased to $-15$ °C, the electrode exhibited a capacity decay rate of 0.05% per cycle with a capacity of 113 mA·h·g$^{-1}$ after 400 cycles (SI Appendix, Fig. S17). Consistent with this performance, the shapes of the discharge/charge profiles were preserved after long-term cycling, and the Mg electrode retained a dendrite-free surface morphology (see Fig. 4D, Inset and SI Appendix, Fig. S18). To the best of our knowledge, the rate capability and cycling stability of the electrode material fabricated in this study were superior to those of all the previously reported inorganic electrode materials for Mg-ion batteries (SI Appendix, Fig. S19 and Table S3). In situ XRD analysis showed that neither phase transformation nor significant volume change occurred during a typical charge/discharge cycle (SI Appendix, Fig. S20), suggesting a zero-strain insertion/extraction of ions. The cross-sectional HR-TEM image of the fully discharged electrode also revealed that the layered structure with a spacing of 1.7 nm was well maintained, although Mg ions were apparently intercalated between the layers.
were all excluded (Fig. 5C). The participation of dissociation/demagnesiation processes (Fig. 5D) suggested that the stripping of Cl ions was likely related to the oxide phase. The primary oxidation state of the pristine electrode was Ti$^{4+}$, while the fully discharged electrode exhibited a shift to low energies and reduction to a valence state near Ti$^{3+}$. This change in the Ti valence state was reversible during the alternate magnesium/demagnesiation processes (Fig. 5B). The participation of oxygen atoms, solvent tetrahydrofuran molecules, and protons were all excluded (Fig. 5C and SI Appendix, Figs. S21 and S22).

The intercalation barrier for the bulky MgCl$^+$ ions with an ionic radius of 0.226 nm in the developed electrode material was sufficient to stabilize the excellent long-term cycling stability of the oxide electrode. Such a quasi-zero-strain characteristic resulted from the pillaring effect of the interlayer alkyl–ammonium ions, which in turn accounted for the excellent long-term cycling stability of the oxide electrode.

In the first discharging, a partial extraction of alkylammonium ions occurred, which produced vacant sites for Mg-intercalation. The results of DFT calculations revealed that the residual amount of C$_8$H$_{16}$N·Ti$_{1.74}$O$_4$ (0.09:1) was sufficient to stabilize the stacking structure with a high interlayer distance of 1.7 nm (SI Appendix, Fig. S23). The amines remained almost intact during the subsequent discharge and charge cycles, and there were no variations in the corresponding signal intensities and chemical compositions, which may help stabilize the structure. Furthermore, the intensities of the $^1$H NMR signals generated by hydroxyl groups and the lattice water remained essentially the same during electrochemical cycling, demonstrating high stability of the lattice water in the electrode structure and also excluding the involvement of protons during the reversible charge and discharge reactions.

Based on these results, it was concluded that the ion storage process likely involved three steps: MgCl$^+$ intercalation, Mg–Cl dissociation into Mg$^{2+}$ and Cl$^-$ ions, and fast Mg$^{2+}$ diffusion in the titanium oxide lattice (Fig. 5A). In almost all Cl-based electrolyte systems, Mg ions typically exist in a complex form (MgCl$^+$ or minor MgCl$_2$$^{2+}$), the dissociation of which requires a high energy of ∼ 3.0 eV. Thus, various MgCl$_2$$^{2+}$ clusters, rather than Mg$^{2+}$ ions, were confirmed to be the active cations participating in the electrochemical reactions when the host lattice possessed a sufficient space to accommodate bulky ions (11, 33, 34). The intercalation barrier for the bulky MgCl$^+$ ions with an ionic radius of 0.226 nm in the developed electrode material was estimated through DFT calculations. A substantial decrease to ∼ 2.7 eV was observed when the interlayer distance exceeded 1.4 nm (Fig. 5D), which roughly corresponds to the accommodation of two layers of MgCl. Experimentally, the amount of Mg ions that could be intercalated into the gallery (intercalation capacity) was strongly dependent on the interlayer distance. For the samples with larger interlayer distances, the amount of intercalated Mg significantly increased under the same measurement conditions (SI Appendix, Figs. S24 and S25). The effect of specific surface was excluded from consideration because all the alkylammonium-spaced specimens possessed similar specific surface areas (SI Appendix, Fig. S26). These results suggest that the expanded interlayer facilitates the direct intercalation of MgCl$^+$ ions during the first step. Subsequently, the compositions of intercalated species in all structures after the full discharge were determined. Regardless of the amine length, divalent Mg$^{2+}$ ions were mainly observed (SI Appendix, Fig. S27), which suggested that the stripping of Cl ions was likely related to the oxide host, probably protons on the oxide sheets. The calculated cleavage energy of Mg–Cl bonds in the presence of H$_2$O$^+$ ions decreased significantly from 2.82 to 0.86 eV, and the bond distance increased by 9% from 0.22 to 0.24 nm (Fig. 5E), indicating a high probability of Mg–Cl dissociation in the presence of protons.
To elucidate the third step of the unusually fast diffusion of divalent Mg\(^{2+}\) ions in oxide lattices, the diffusion energy barrier was calculated (Fig. 5F and SI Appendix, Fig. S28). Because titanium oxide sheets were stacked in a disordered manner over large distances, the transport behavior of Mg\(^{2+}\) ions across a titanium oxide sheet was considered. It was found that these ions preferred atomic troughs in the lattice as diffusion pathways with an energy barrier below 0.1 eV. Moreover, the top region of the minimum energy path for the Mg\(^{2+}\) transport along this direction was essentially flat. Across the atomic troughs, the diffusion barriers of Mg\(^{2+}\) ions significantly increased to 0.6 eV, although the top region of the minimum energy paths remained flat.

Fig. 5. Mechanism for genuine Mg\(^{2+}\) intercalation and fast diffusion. (A) Schematic illustration of the mechanism of Mg\(^{2+}\) storage and fast diffusion in the designed oxide electrode evaluated using PhMgCl\(_2\)-AlCl\(_3\) electrolyte. (B) XANES spectra of the designed titanium oxide electrode recorded at the Ti K-edge in different charged and discharged states. (C) \(^1\)H NMR spectra of the pristine, discharged, and charged electrodes. (D) Intercalation barrier of MgCl\(^+\) ions plotted as a function of the interlayer distance. (E) Desolvation energy of MgCl\(_2\) species and the related change in their bond length. (F) Potential-energy surfaces obtained for Mg\(^{2+}\) and MgCl\(^+\) ions along different diffusion paths. (G) Electronic density profiles of the titanium oxide structure. (H) Electronic density profiles of the titanium oxide structure with the added Mg atoms and the corresponding differences in the charge density. Red: charge accumulation, blue: charge depletion.

To elucidate the third step of the unusually fast diffusion of divalent Mg\(^{2+}\) ions in oxide lattices, the diffusion energy barrier was calculated (Fig. 5F and SI Appendix, Fig. S28). Because titanium oxide sheets were stacked in a disordered manner over large distances, the transport behavior of Mg\(^{2+}\) ions across a titanium oxide sheet was considered. It was found that these ions preferred atomic troughs in the lattice as diffusion pathways with an energy barrier below 0.1 eV. Moreover, the top region of the minimum energy path for the Mg\(^{2+}\) transport along this direction was essentially flat. Across the atomic troughs, the diffusion barriers of Mg\(^{2+}\) ions significantly increased to 0.6 eV, although the top region of the minimum energy paths remained flat.
Unfortunately, for the diffusion of MgCl\textsuperscript{+} ions with a lower charge density, this surface did not provide any benefits. The MgCl\textsuperscript{+} diffusion barrier was higher than that for Mg\textsuperscript{2+} ions along the atomic troughs, and a high singlet barrier of 0.5 eV was detected for the former species, inhibiting its fast migration. By a comparison with reported materials, it was noted that the energy barrier for the Mg\textsuperscript{2+} migration across the titanium oxide sheet in this study was lower than that of the Mg\textsuperscript{2+} diffusion across TiS\textsubscript{2} (11), MoS\textsubscript{2} (35), and even MoO\textsubscript{3}S\textsubscript{2} (36) (the latter represents a well-known material with anomalously fast Mg\textsuperscript{2+} transport). The electronic origins of fast Mg\textsuperscript{2+} diffusion were investigated via density analysis, and the obtained results are presented in Fig. 5 G and H. The sp electrons in the analyzed titanium oxides were preferentially “spilled-out” along the atomic troughs owing to the anisotropic Smoluchowski effect. This effect became more pronounced with the addition of Mg\textsuperscript{2+} ions at both the hollow and bridge sites along the troughs. The extension of the wavefunction induced the formation of flat potential-energy surfaces along the atomic troughs, thereby providing a solid foundation for the unusually fast Mg\textsuperscript{2+} diffusion in this direction. This also fundamentally explains the absence of MgO formation during Mg\textsuperscript{2+} intercalation and diffusion. Electrochemical impedance spectra indicate a significant decrease in the radius of the semicircle beyond the high-medium frequency region due to Mg\textsuperscript{2+} intercalation, implying a small charge transfer resistance and high probability of achieving fast reaction kinetics (SI Appendix, Fig. S29). The spill-out of electrons changed the electron distribution and surface polarizability, which in turn caused a slight structural distortion in the Ti coordination of Ti-O and Ti-Ti bonds (SI Appendix, Fig. S30). The lattice water and/or hydroxyl groups might also help screen Coulombic charges, and the dehydrated sample possessed lower discharge and charge capacities and rate capabilities (SI Appendix, Fig. S31). Hence, the unique electrode surface and low diffusion energy barrier account for the fast diffusion of bare Mg\textsuperscript{2+} ions at room and even subzero temperatures.

Intriguingly, the proton-assisted technique utilized to achieve genuine divalent Mg-ion storage can be generally applied to other two-dimensional materials, including manganese oxide and oxygen-terminated titanium carbide (SI Appendix, Figs. S32–S35).

In these cases, the predominant intercalating species switched from MgCl\textsuperscript{+} to Mg\textsuperscript{2+} with the incorporation of protons into the gallery. In addition, the diffusivity of divalent Mg\textsuperscript{2+} ions was comparable to that of monovalent MgCl\textsuperscript{+} ions, exhibiting no apparent degradation in the migration rate.

In summary, both genuine intercalation and fast diffusion of divalent Mg ions were achieved in metal oxides not only at room temperature but also at a subzero temperature in the present study. The proposed strategy involved placing protons on metal-oxide sheets and stacking these sheets over a large distance in a disordered manner. The high distance promoted the intercalation of Mg complexes; the protons triggered the cleavage of the Mg–Cl bond; and the anisotropic Smoluchowski effect (the wavefunction expansion in the atomic trough of the titanium oxide lattice) produced flat potential-energy surfaces, which enabled unusually fast diffusion of divalent Mg\textsuperscript{2+} species with a record Mg-ion conductivity of 1.8 × 10\textsuperscript{–4} S cm\textsuperscript{–1} at a room temperature of 25 °C. As a result, a high-power Mg-ion battery that maintains the high-energy profit was obtained. Practically, the cell that was charged in 55 s could be gradually discharged for a stable long run of ~4.5 h. Importantly, the demonstrated approach can be extended to other two-dimensional sheet materials, representing a general strategy for designing high-performance electrodes for multivalent metal-ion batteries with superior diffusion characteristics.

Materials and Methods

Experimental details on the procedures of preparing titanium oxide sheets and n-alkylammonium-ion-spaced oxide specimens, structural characterization, collecting electrochemical performance data, calculating the diffusion coefficient, estimating energy and power densities, and the settings for theoretical simulations are provided in SI Appendix.

Data Availability. All study data are included in the article and/or SI Appendix.

ACKNOWLEDGMENTS. We acknowledge financial support from the National Natural Science Foundation of China (Grant 51772201 and 52173288). We also thank Xiao Han and Prof. Pengfei Yan at Beijing University of Technology for their support with in situ XRD measurement.

1. Y. Liang, H. Dong, D. Aurbach, Y. Yao, Current status and future directions of multivalent metal-ion batteries. Nat. Energy 5, 646–656 (2020).
2. M. Li et al., Design strategies for nonaqueous multivalent-ions and monovalent-ion oxidation reduction materials. Nat. Rev. Mater. 5, 276–294 (2020).
3. D. Aurbach et al., Prototype systems for rechargeable magnesium batteries. Nature 407, 724–727 (2000).
4. J. Muldoon, C. B. Bucur, T. Gregory, Quest for nonaqueous multivalent secondary batteries. Magnesium and beyond. Chem. Rev. 114, 11683–11720 (2014).
5. H. D. Yoo et al., Mg rechargeable batteries: An on-going challenge. Energy Environ. Sci. 6, 2265–2279 (2013).
6. P. Canepa et al., Odyssey of multivalent cathode materials: Open questions and future challenges. Chem. Rev. 117, 4287–4341 (2017).
7. E. Levi, Y. Gofer, D. Aurbach, On the way to rechargeable Mg batteries: The challenge of new cathode materials. Chem. Mater. 22, 860–868 (2010).
8. L. F. Wan, B. R. Perdue, C. A. Apldett, D. Prendergast, Mg deolviation and intercalation mechanism at the MoS\textsubscript{2} chevrel phase surface. Chem. Mater. 27, 5932–5940 (2015).
9. Z. Li et al., Fast kinetics of multivalent intercalation chemistry enabled by solvated magnesium-ions into self-established metallic layered materials. Nat. Commun. 9, 5115 (2018).
10. X. Ji et al., Water-activated VOPO\textsubscript{4} for magnesium ion batteries. Nano Lett. 18, 6441–6448 (2018).
11. H. D. Yoo et al., Fast kinetics of magnesium monochloride cations in interlayer-expanded titanium disulfide for magnesium rechargeable batteries. Nat. Commun. 8, 339 (2017).
12. H. Dong et al., High-power Mg batteries enabled by heterogeneous etolization redox chemistry and weakly coordinating electrolytes. Nat. Energy 5, 1043–1050 (2020).
13. P. Canepa et al., High magnesium mobility in ternary spinel chalcopyrides. Nat. Commun. 8, 1759 (2017).
14. T. S. Arthur et al., Understanding the electrochemical mechanism of K\textsubscript{4}MnO\textsubscript{4} for magnesium battery cathodes. ACS Appl. Mater. Interfaces 6, 7004–7008 (2014).
15. L. Wang, T. Sasaki, Titanium oxide nanosheets: Graphene analogues with versatile functionalities. Chem. Rev. 114, 9455–9486 (2014).
16. T. Sasaki, M. Watanabe, H. Hashizume, H. Yamada, H. Nakazawa, Macromolecule-like aspeks for a colloidal suspension of an exfoliated titanate. pairwise association of nanosheets and dynamic reassembly process initiated from it. J. Am. Chem. Soc. 118, 8329–8335 (1996).
17. J. Yang et al., Size-independent fast ion intercalation in two-dimensional titanate nanosheets for alkali-metal-ion batteries. Angew. Chem. Int. Ed. Engl. 58, 8740–8745 (2019).
18. F. Menéndez, A. Espina, C. Trojabo, J. Rodríguez, Intercalation of n-alkylamines by lamellar materials of the u-zirconium phosphate type. Mater. Res. Bull. 25, 1531–1539 (1990).
19. M. Kitano et al., Protonated titanate nanotubes with Lewis and Brensted acidity: Relationship between nanotube structure and catalytic activity. Chem. Mater. 25, 385–393 (2013).
20. A. M. Tripathi, W.-N. Su, B. J. Hwang, In situ analytical techniques for battery interface analysis. Chem. Soc. Rev. 47, 836–851 (2018).
21. J. Lee, I. D. Seymour, A. J. Pell, S. E. Dutton, C. G. Grey, A systematic study of 92-Mg NMR in paramagnetic transition metal oxides: Applications to Mg-ion battery materials. Phys. Chem. Chem. Phys. 19, 613–625 (2016).
22. C. Bai et al., Interchain-expanded vanadium tetrasulfide with fast kinetics for rechargeable magnesium batteries. ACS Appl. Mater. Interfaces 11, 31598–31619 (2019).
23. X. Sun et al., A high capacity thiospinel cathode for Mg batteries. Energy Environ. Sci. 9, 2273–2277 (2016).
24. M. D. Levi et al., Phase transitions and diffusion kinetics during Mg\textsuperscript{2+} and Li\textsuperscript{+} insertions into the MoS\textsubscript{2} chevrel phase compound studied by PIITT. Electrochim. Acta 49, 3201–3209 (2004).
25. T. Koketsu et al., Reversible magnesium and aluminium ions insertion in cation-deficient anate TiO\textsubscript{2}. Nat. Mater. 16, 1142–1148 (2017).
26. C. Chen, J. Wang, G. Zhao, Y. Wang, J. Chen, Layered Na\textsubscript{4}Ti\textsubscript{3}O\textsubscript{7}·MgNaTi\textsubscript{3}O\textsubscript{7}·Mg\textsubscript{2}Na\textsubscript{2}Ti\textsubscript{2}O\textsubscript{5} nanoribbons as high-performance anode of rechargeable Mg-ion batteries. ACS Energy Lett. 1, 1165–1172 (2016).

Genuine divalent magnesium-ion storage and fast diffusion kinetics in metal oxides at room temperature

Yang et al.
27. X. Xue et al., One-step synthesis of 2-ethylhexylamine pillared vanadium disulfide nanoflowers with ultralarge interlayer spacing for high-performance magnesium storage. Adv. Energy Mater. 9, 1900145 (2019).

28. Q. Liu et al., Approaching the capacity limit of lithium cobalt oxide in lithium ion batteries via lanthanum and aluminium doping. Nat. Energy 3, 936–943 (2018).

29. S. Yang et al., Determination of the chemical diffusion coefficient of lithium ions in spherical Li(Ni0.5Mn0.3Co0.2)O2. Electrochim. Acta 66, 88–93 (2012).

30. L. A. Montoro, J. M. Rosolen, The role of structural and electronic alterations on the lithium diffusion in LiCoO2-NiO2. Electrochim. Acta 49, 3243–3249 (2004).

31. X. Rui, N. Ding, J. Liu, C. Li, C. Chen, Analysis of the chemical diffusion coefficient of lithium ions in Li2V2(PO4)3 cathode material. Electrochim. Acta 55, 2384–2390 (2010).

32. S. Rasul, S. Suzuki, S. Yamaguchi, M. Miyayama, High capacity positive electrodes for secondary Mg-ion batteries. Electrochim. Acta 82, 243–249 (2012).

33. L. Zhou et al., Interlayer-spacing-regulated VOPO4 nanosheets with fast kinetics for high-capacity and durable rechargeable magnesium batteries. Adv. Mater. 30, e1801984 (2018).

34. L. F. Wan, D. Prendergast, The solvation structure of Mg ions in dichloro complex solutions from first-principles molecular dynamics and simulated X-ray absorption spectra. J. Am. Chem. Soc. 136, 14456–14464 (2014).

35. Y. Liang et al., Interlayer-expanded molybdenum disulfide nanocomposites for electrochemical magnesium storage. Nano Lett. 15, 2194–2202 (2015).

36. C. Ling, K. Suto, Thermodynamic origin of irreversible magnesium trapping in Chevrel phase Mo6S8: Importance of magnesium and vacancy ordering. Chem. Mater. 29, 3731–3739 (2017).