Thermal Percolation of Antiperovskite Superionic Conductor into Porous MXene Scaffold for High-Capacity and Stable Lithium Metal Battery

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1. Introduction

Lithium metal battery is considered an emerging energy storage technology due to its high theoretical capacity and low electrochemical potential. However, the practical exploitations of lithium metal batteries are not realized because of uncontrollable lithium deposition and severe dendrite formation. Herein, a thermal percolation strategy is developed to fabricate a dual-conductive framework using electronically conductive Ti$_3$C$_2$T$_x$ MXene aerogels (MXAs) and Li$_2$OHCl antiperovskite superionic conductor. By melting Li$_2$OHCl at a low temperature, the molten antiperovskite phase can penetrate the MXA scaffold, resulting in percolative electron/ion pathways. Through density functional theory calculations and electrochemical characterizations, the hybridized lithiophilic (MXA)–lithiophobic (antiperovskite) interfaces can spatially guide the deposition of lithium metals and suppress the growth of lithium dendrites. The symmetric cell with MXA–antiperovskite electrodes exhibits superior cycling stability at high areal capacities of 4 mAh cm$^{-2}$ over 1000 h. Moreover, the full cell with MXA–antiperovskite anode and high-loading LiFePO$_4$ cathode demonstrates high energy and power densities (415.7 Wh kg$_{\text{cell}}^{-1}$ and 231.0 W kg$_{\text{cell}}^{-1}$) with ultralong lifespans. The thermal percolation of lithium superionic conductor into electronically conductive scaffolds promises an efficient strategy to fabricate dendrite-free lithium metal anodes with high energy/power densities.
interfaces between lithium metal and organic liquid electrolyte. First, electronically conductive 3D scaffolds (e.g., carbon,[3] metal-based,[4] and Ti3C2Tx MXene[5]) have been utilized to dissipate electrons at the anode/electrolyte interfaces during the battery-charging process. However, as illustrated in Figure 1a, fast combination between Li+ and electron leads to uneven lithium deposition with problematic dendrites and dead phases at the scaffold’s top surface. Another approach is to incorporate an ionically conductive protection layer (e.g., LiF interphase layers[6] and superionic conductor coatings[7]), which can modulate Li+ distribution on the host material. However, inorganic ionic conductors are normally fragile and prone to fracture during lithium plating/stripping (Figure 1b), and polymeric ionic conductors suffer from low mechanical moduli, which cannot suppress lithium dendrite growth.[8] An emerging approach is to develop a dual-conductive electrode, enabling homogeneous electron/Li+ distribution during lithium plating/stripping (Figure 1b), and polymeric ionic conductors suffer from low mechanical moduli, which cannot suppress lithium dendrite growth.[8] An emerging approach is to develop a dual-conductive electrode, enabling homogeneous electron/Li+ distribution during lithium plating/stripping. However, the reported anode hosts with Li+-transporting pathways were fabricated with dispersed superionic conductor phases (e.g., LiLaZrAlO[9] and Li3N[10]), which did not form continuous ionically conductive pathways and showed unsatisfied capacities and rate performance.[11] For the dual-conductive electrodes developed with lithium defects (e.g., Li,Si–Li2O[12] and Li,Mg[13]), the batteries showed short-term lifespans because these lithium defects tended to be inactivated and disappear during repeated lithium plating/stripping processes.

Herein, a dual-conductive framework with percolative electron/Li+ pathways was constructed by incorporating Li2OHCl antiperovskite superionic conductor into electronically conductive Ti3C2Tx MXene aerogels (MXAs) via a thermal percolation strategy (Figure 1c). Li2OHCl exhibits a low melting point (at ≈ 300 °C) and high ionic conductivity (10−3 S cm−1 at the room temperature), which is highly feasible to be integrated into an electronically conductive scaffold.[14] As illustrated in Figure 1d,e, by integrating Li2OHCl antiperovskite into MXAs followed by in situ thermal penetration at 300 °C, a MXA–antiperovskite framework with percolative electron/ion pathways was fabricated in a controllable and scalable fashion. Through density functional theory (DFT) calculations and electrochemical characterizations, the dual-conductive MXA–antiperovskite framework exhibited hybridized lithiophilic (MXA)–lithiophobic (antiperovskite) interfaces, which confined lithium metal deposition in the MXA’s micropores and prevented random dendrite growth. The symmetric cell with two MXA–antiperovskite electrodes exhibited ultralong and stable cyclic performance (>1000 h) at high areal capacities of 4 mAh cm−2. Moreover, the full cell with MXA–antiperovskite anode and high-loading LiFePO4 cathode (12 mg cm−2) in the commercial carbonate electrolyte demonstrated high energy densities (415.7 Wh kgcell−1) and power densities (231.0 W kgcell−1) with superior cycling stability. The thermal percolation of lithium superionic conductor into electronically conductive scaffolds promises an efficient strategy to fabricate dual-conductive electrodes, which benefits the development of dendrite-free and stable lithium metal anodes with high energy/power densities.

Figure 1. Morphological evolutions of lithium metal in various host materials. a) Electronically conductive scaffold that leads to serious formation of lithium dendrites. b) Superionic conductor coating that leads to surface cracks and lithium dendrites. c) Electron/ion dual-conductive framework that spatially regulates lithium metal deposition. d) Thermal percolation of molten antiperovskite phase into a porous MXA scaffold. e) Antiperovskite-infiltrated MXA framework with percolative electron/ion pathways.
2. Results and Discussion

2.1. Rational Design of Dual-Conductive MXA–Antiperovskite Framework

Ti$_3$C$_2$T$_x$ MXene (MXene) nanosheets with superior electronic conductivities, high flexibility, and lithiophilic functional groups are suitable for the fabrication of 3D, conductive scaffolds that facilitate the electron transporting processes for lithium plating/stripping.\cite{15} Figure 2a shows the transmission electron microscope (TEM) image of Ti$_3$C$_2$T$_x$ MXene nanosheets, and the X-ray diffraction (XRD) patterns are provided in Figure S1, Supporting Information. By introducing an alkaline solution into the MXene dispersion, the MXene nanosheets were ionically assembled. Followed by a freeze-drying process, Ti$_3$C$_2$T$_x$ MXene aerogels (abbreviated as MXAs) were able to be fabricated (see details in Experimental Section). As shown in Figure 2b; Figure S2, Supporting Information, the as-prepared MXA was hierarchical and exhibited open micropores and interconnected channels.

On the other hand, Li$_2$OHCl is an antiperovskite superionic conductor and has a relatively lower melting point (at $\approx$300 °C, the cubic crystalline structure in Figure 2c) than other reported superionic conductors (such as oxide-based garnets and argyrodite-type sulfides with high sintering/melting temperatures $>$500 °C).\cite{16} In addition, Li$_2$OHCl demonstrates high ionic conductivity ($10^{-3}$ S cm$^{-1}$), interfacial stability with lithium metal, and superior mechanical strength (Young's modulus: 43.2 GPa), all of which can be harnessed to suppress the growth of lithium dendrites.\cite{14,17} Li$_2$OHCl was synthesized by first grinding lithium hydroxide (LiOH) with lithium chloride (LiCl) followed by sintering at 400 °C. After overnight cooling and ball milling, Li$_2$OHCl superionic conductor was obtained with its XRD pattern characterized in Figure 2c.

Figure 2. Rational design of dual-conductive MXA–antiperovskite framework. a) TEM image and crystalline structure of Ti$_3$C$_2$T$_x$ MXene nanosheets. b) SEM image of a MXA scaffold. c) XRD pattern and crystalline structure of Li$_2$OHCl antiperovskite. d) Cross-section SEM image, EDS mapping, digital photograph (inset) of a MXA–antiperovskite framework (on a copper foil). e) Cross-section SEM image and f) EDS mapping of MXA–antiperovskite framework at larger magnifications. g) DFT-calculated binding energies at MXene||Li$_2$OHCl interfaces at 0, 298, and 600 K. Insets show the relaxed sandwiched structure of a Li$_2$OHCl||MXene||Li$_2$OHCl model at 0 and 600 K. h) DFT-calculated binding energies at Li||Li$_2$OHCl and Li||MXene interfaces. Insets are the relaxed sandwiched structures of Li||Li$_2$OHCl||Li and Li||MXene||Li models at 0 K.
A thermal percolation process was developed for the fabrication of a dual-conductive MXA–antiperovskite framework. First, MXA powders and Li₂OHCl crystals were both dispersed in N-methyl pyrrolidone (NMP), and a binder-free slurry was formed and then coated onto a copper foil followed by drying in an argon glovebox. Afterward, the MXA–antiperovskite composite was heated up to ~300 °C, at which the molten antiperovskite phase penetrated the MXA's scaffolds (Figure 1d). The mass ratio of Li₂OHCl phase presented essential influences on the formation of percolative electron/ion pathways. Different anode hosts were prepared with different MXA-to-Li₂OHCl ratios and their Coulombic efficiencies of lithium plating/stripping were tested in the asymmetric cells with the mild ether electrolyte (1.0 M LiTFSI in DOL/DME with 1.0 wt% LiNO₃, relatively stable with lithium metal[22c-138]). The Coulombic efficiency was defined as the ratio of stripped lithium amount versus deposited lithium amount in a lithium plating/stripping cycle, reflecting reversibility of lithium plating/stripping during the cycling tests (Equation (1)).

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\text{Coulombic Efficiency} = \frac{\text{Stripped Capacity}}{\text{Deposited Capacity}} \times 100\% \quad (1)
\]

As shown in Figure S3, Supporting Information, when the MXA-to-Li₂OHCl ratio was 3:1, the Coulombic efficiencies showed rapid drops with increasing cycle numbers. This was due to the fact that the Li₂OHCl phase did not form ionically percolative pathways within the MXA scaffold. When the MXA-to-Li₂OHCl ratio increased to 2:1, the asymmetric cell demonstrated high and stable Coulombic efficiencies over 80 cycles. However, when the MXA-to-Li₂OHCl ratio increased to 1:1, the Coulombic efficiencies became less cycle-stable, as the electronically conductive pathways (MXA phase) were blocked by the ionically conductive Li₂OHCl phase. Therefore, the MXA-to-Li₂OHCl ratio was optimized at 2:1 in this work. The XRD pattern of MXA–antiperovskite framework with characteristic MXene peaks and Li₂OHCl cubic phase is provided in Figure S4, Supporting Information. As shown in the cross-section scanning electron microscopy (SEM) image and the energy dispersive spectroscopy (EDS) mapping (Figure 2d), the antiperovskite phase (with Cl signals) was present uniformly across the MXA scaffold (with Ti signals). The MXA–antiperovskite framework exhibited crumple-like porous structures with high flexibility (Figure 2d,e), providing additional spaces to accommodate large volume variations during reversible lithium plating/stripping.[3b,c,4a] Notably, the EDS mapping in Figure 2f indicated that the thermal percolation process enabled interfacial hybridization between antiperovskite phase and MXene nanosheet in nanoscale; thus, providing continuous ionic transporting networks for Li⁺.

The vertical distribution of antiperovskite phase was investigated by X-ray photoelectron spectroscopy (XPS) depth-profiling in Figure S5, Supporting Information. As the etching depth increased to 400 nm, the peak intensities of Ti−C, Ti−O, and Ti−F (from MXAs) and Cl 2p (from Li₂OHCl) remained unchanged, showing percolated antiperovskite phase throughout the MXA scaffold. The ionic conductivity of MXA–antiperovskite framework was measured by using electrochemical impedance spectroscopy (EIS), based on the reported protocols (see calculation details in Note S1, Supporting Information).[11a,19] As shown in the Nyquist plot (Figure S6, Supporting Information), the ionic conductivity of a MXA–antiperovskite framework was characterized to be 1.62 × 10⁻² S cm⁻¹ at the room temperature, which is much higher than some reported NaSICON-, and garnet-type ionic conductors.[26]

Next, the interfacial interactions between MXene nanosheets and Li₂OHCl antiperovskite were investigated using density functional theory (DFT) calculation and ab initio molecular dynamics (AIMD) simulation. As shown in Figure 2g, a relaxed MXene model was sandwiched between two Li₂OHCl supercells (interact with [111] cleaved plane with the lowest surface energy, Figure S7, Supporting Information), which was named as Li₂OHCl||MXene||Li₂OHCl. As the temperature increased from 0 to 600 K, the binding energy at the Li₂OHCl||MXene interfaces decreased from ~1.38 eV to ~2.64 eV. With the negative binding energy at 600 K, the molten Li₂OHCl phase theoretically exhibited spontaneous adsorption and superior wettability on the MXene surfaces. Figure S8, Supporting Information, shows experimental evidence that the molten antiperovskite was able to infiltrate into an electronically conductive MXA scaffold when the temperature increased to 300 °C.

By calculating the binding energies at Li||MXene and Li||Li₂OHCl interfaces, the suppression effects of MXA–antiperovskite framework on the growth of lithium dendrites were theoretically evaluated.[30] As shown in Figure 2h, a relaxed MXene model was established between two lithium metal phases (interact with [111] cleaved plane with the lowest surface energy, Figure S9, Supporting Information), which was named as Li||MXene||Li. Similarly, a Li₂OHCl supercell was sandwiched between two lithium metal phases, which was named as Li||Li₂OHCl||Li (inset of Figure 2h). The binding energies in the Li||MXene||Li model were calculated to be ~0.781 eV, while the binding energies at the Li||Li₂OHCl||Li model were calculated to be 0.591 eV. The DFT results indicated that the MXA scaffold was lithiophobic, which could promote uniform lithium plating with lower lithium nucleation barrier.[24] In contrast, the Li₂OHCl antiperovskite was lithiophobic (with the experimental evidence in Figure S10, Supporting Information), which could regulate random lithium deposition; and thus, suppress dendritic lithium growth.[22] The MXA–antiperovskite framework with hybridized lithiophilic–lithiophobic interfaces was expected to serve as an ideal host material for lithium metal anode.

2.2. Confined Deposition of Lithium Metals With High Coulombic Efficiencies in MXA–Antiperovskite Frameworks

During reversible lithium plating/stripping process, the morphological evolution of a dual-conductive MXA–antiperovskite framework was investigated via ex situ SEM. The MXA–antiperovskite framework coated on copper foil was utilized as a working electrode in an asymmetric cell with the ether electrolyte, and lithium metal was placed as a counter electrode. Comparing with the SEM image before lithium deposition (Figure S11a, Supporting Information), homogeneous lithium deposits with mosaic-like morphologies were observed on the
MXA–antiperovskite electrode in Figure 3a. In comparison, the MXA–only electrode demonstrated uneven lithium metal surface (Figure 3b) due to the accumulation of electrons at its top surface. After lithium deposition, the uniform surface of antiperovskite–only electrode in Figure S11c, Supporting Information, was broken up into small pieces because of large interfacial volume changes (Figure 3c).

As the areal capacity of deposited lithium increased from 1 to 4 mAh cm$^{-2}$, the lithium-deposited MXA–antiperovskite framework became thicker from 10 to 50 µm (marked with arrows in the cross-section SEM images in Figure 3d–f). Furthermore, the time-of-flight secondary ion mass spectroscopy (ToF SIMS) with cross-section mapping was conducted to investigate the deposition depth of lithium metals. As demonstrated in Figure 3g,h, strong lithium signals (i.e., Li$^+$) were present across the entire MXA–antiperovskite framework (50-µm-thick), showing that metallic lithium deposits were conformally confined within the MXA–antiperovskite's micropores. Notably, after 50 cycles of lithium plating/stripping at high areal capacities of 4 mAh cm$^{-2}$, the MXA–antiperovskite electrode remained a smooth lithium surface (SEM images in Figure 3i) and lithium-filled MXA scaffold (Figure 3j) served as an ideal host material for lithium metal anode. In contrast, the MXA–only electrode (after 30 cycles at 4 mAh cm$^{-2}$) showed un-filled MXA scaffold with severe lithium dendrites (SEM images in Figure 3k,l), which eventually became inactive and dead lithium phases. These studies of ToF SIMS and ex situ SEM demonstrated that the MXA–antiperovskite framework was able to regulate lithium deposition.
from two aspects. The first aspect was through forming hybrid-ized lithiophilic (MXA)--lithiophobic (antiperovskite) interfaces in the framework. As illustrated in Figure S12, Supporting Information, the lithium nucleation majorly occurred on the lithiophilic MXA scaffold, where Li\(^+\) migrated through the ionic conductive Li\(_2\)OHCl phase and got reduced on the proximal uncoated MXA surfaces. During the growth of lithium deposits, the surrounded lithiophobic Li\(_2\)OHCl phase was able to suppress lithium dendrites and spatially limit their growth. Another aspect originated from the high Young's modulus of antiperovskite Li\(_2\)OHCl phase (43.2 GPa), which blocked the penetration of upward-growing dendritic lithium.

Figure 4a demonstrates the Coulombic efficiencies of MXA--antiperovskite (with and without thermal percolation), MXA-only, antiperovskite-only, and bare copper electrodes in the asymmetric cells with the ether electrolyte. After thermal percolation at 300 °C, the MXA--antiperovskite electrode demonstrated high and stable Coulombic efficiencies (>99.4%) over 200 cycles at the areal capacities of 1 mA h cm\(^{-2}\). In contrast, without thermal percolation, the MXA--antiperovskite electrode exhibited inefficient and fluctuating Coulombic efficiencies lower than ≈80%, as the poor electrode electronic/ionic conductivities and inhomogeneous interphases between MXA and randomly distributed Li\(_2\)OHCl powder disrupted the reversibility of lithium plating/stripping. In control experiments, the asymmetric cell with an antiperovskite--only electrode was dead after a few cycles due to the propagation of surface cracks (SEM image in Figure S13a, Supporting Information). Although stable lithium plating/striping behaviors were observed at the very beginning, the asymmetric cell with either MXA-only or bare copper electrode showed dramatic efficiency decays after 50–60 cycles because of the formation of lithium dendrites (SEM images in Figure S13b,c, Supporting Information). Moreover, the asymmetric cell with a MXA--antiperovskite electrode demonstrated stable Coulombic efficiencies (>99.5%) over 130 cycles even at higher areal capacities up to 4 mA h cm\(^{-2}\) (Figure 4b). In comparison, both asymmetric cells (with a MXA--only electrode and with a bare copper electrode) experienced fast efficiency decays after several dozen cycles as severe lithium dendrites and dead lithium phases were developed on the working electrodes (SEM images in Figure S14, Supporting Information).

In addition, the lithium plating/striping reversibility of MXA--antiperovskite electrode in the commercial carbonate electrolyte (1.0 M LiPF\(_6\) in EC/DMC/DEC) was tested in Figure S15, Supporting Information. In the commercial electrolyte with no additives, the asymmetric cells with MXA--antiperovskite electrode showed stable cyclic performance with high Coulombic efficiencies at the areal capacities of 1 and 4 mA h cm\(^{-2}\),
whereas the other control electrodes showed poor reversibility with large fluctuations.

2.3. Performance of MXA–Antiperovskite Electrodes in Symmetric Cells

Next, the MXA–antiperovskite framework was transferred onto an active lithium foil by sequential rolling and pressing processes for the fabrication of a MXA–antiperovskite electrode (Figure S16, see details in Experimental Methods), as well as the fabrication of MXA–only and antiperovskite–only control electrodes on lithium foils. A pair of MXA–antiperovskite electrodes (on lithium foil) were then assembled into a symmetric cell to characterize the electrode/electrolyte interfacial stability in the ether electrolyte or the commercial carbonate electrolyte. As shown in Figure 4c, the symmetric cell with the ether electrolyte demonstrated stable galvanostatic cycling and a long lifespan over 1200 hours at 1 mAh cm$^{-2}$. At higher areal capacities of 4 mAh cm$^{-2}$, the symmetric cell still achieved stable galvanostatic cycling over 1000 hours, and the voltage polarization remained small (<35 mV, inset of Figure 4d). On the other hand, three symmetric cells with bare lithium, MXA–only, and antiperovskite–only electrodes were fabricated for the control experiments. All three symmetric cells showed short lifespans with fast increased voltage polarizations (>120 mV, inset of Figure 4c) at the areal capacities of 1 mAh cm$^{-2}$. If operated at the higher areal capacities of 4 mAh cm$^{-2}$, the cells were short-circuited in less than 200 hours due to severe dendrite formation (Figure 4d).

Meanwhile, compared with the other three control electrodes, the symmetric cells using MXA–antiperovskite electrodes in the commercial carbonate electrolyte still displayed high cyclic stability with small voltage polarizations at the areal capacities of both 1 and 4 mAh cm$^{-2}$ (Figure S17, Supporting Information). As shown in Figure S18, Supporting Information, the rate performance of symmetric cells using different electrodes in the two kinds of electrolytes was further tested at the fixed areal capacities of 1 mAh cm$^{-2}$. Compared with the other three control electrodes, the cells with MXA–antiperovskite electrodes delivered the smallest voltage-hysteresis changes in both electrolytes at different rates of 1, 2, 3, 4, and 5 mA cm$^{-2}$, respectively. However, the cells using antiperovskite–only electrodes experienced drastic voltage fluctuations at high rates (3–5 mA cm$^{-2}$) and large voltage polarizations were observed in the symmetric cells with MXA–only electrodes.

EIS measurements were conducted on the symmetric cells with the ether electrolyte to analyze the interfacial stability between electrode and electrolyte during the galvanostatic cycling. Figure 4e presents the Nyquist plots of two kinds of symmetric cells (one with MXA–antiperovskite electrodes, one with bare lithium electrodes) after 50, 100, and 150 cycles of lithium plating/stripping at the areal capacities of 1 mAh cm$^{-2}$ at 1 mA cm$^{-2}$. The EIS results were fitted using an equivalent circuit in Figure S19, Supporting Information, and the fitted component values were summarized in Table S1, Supporting Information. The symmetric cell with bare lithium electrodes showed the charge transfer resistance ($R_t$) decreasing from 9.05 Ω (50 cycles) to 3.87 Ω (150 cycles) mainly due to the accumulation of lithium dendrites (as evidenced in Figure S21, Supporting Information). In contrast, during the galvanostatic cycling, the symmetric cell with MXA–antiperovskite electrodes demonstrated cycle-stable $R_t$ values, which slightly decreased from 2.78 Ω (50 cycles) to 2.39 Ω (150 cycles). The EIS results implied that the MXA–antiperovskite electrode exhibited superior interfacial stability by suppressing the irreversible corroded reactions between active lithium and electrolyte.

The morphological evolution of a MXA–antiperovskite electrode (on lithium foil) during lithium deposition was further investigated via ex situ SEM. As shown in the side-view and top-down SEM images (Figure S20a–c, Supporting Information), the porous MXA–antiperovskite framework was successfully transferred onto a lithium foil. As shown in Figure S20e, Supporting Information, with 1 mAh cm$^{-2}$ lithium deposits, the top half of the MXA–Li$_2$OCl framework was filled with mosaic-like lithium metals, while the bottom half close to the lithium foil was unfilled. The results indicated that the lithium nucleation and growth in the symmetric cells was consistent with the deposition behaviors in the asymmetric cells (Figure S12, Supporting Information). Moreover, the MXA–antiperovskite electrodes (harvested from the symmetric cell) still exhibited flat and smooth lithium metal surface after 150 cycles of lithium plating/stripping (SEM image in Figure 4f,g). In comparison, the bare lithium electrodes (harvested from the symmetric cell) showed a much rougher surface with lithium protuberances (SEM image in Figure S21, Supporting Information). The SEM results further proved that the MXA–antiperovskite framework homogenized the distribution of electrodes/ions and thus, led to uniform and confined lithium metal deposition. Figure 4h compares the symmetric-cell performance of our MXA–antiperovskite electrodes with other dual-conductive electrodes and MXene-based hosts in the literature; detailed comparison is provided in Tables S2 and S3, Supporting Information, respectively. Compared to most of the reported symmetric-cell performances (e.g., low areal capacities of ≤1 mAh cm$^{-2}$ and limited cycling performance ≤700 h), the MXA–antiperovskite electrode demonstrated superior cycling stability up to 1000 h in a symmetric cell at high areal capacities up to 4 mAh cm$^{-2}$, benefiting from its hierarchical structures with hybridized lithiophilic–lithiophobic interfaces and continuous dual-conducting pathways.

2.4. Performance of MXA–Antiperovskite Anodes in Full Cells

For practical battery applications, a full cell was finally fabricated using a MXA–antiperovskite framework on a lithium foil as the anode and a high-loading LiFePO$_4$ cathode (12 mg cm$^{-2}$). Either the ether electrolyte or the commercial carbonate electrolyte was used for the as-fabricated full cell. First of all, the ether electrolyte was adopted to fabricate full cells using 200-μm-thick lithium foils, and the resultant full cells were named as MXA–antiperovskite cells. Meanwhile, the full cells with bare lithium anodes were also fabricated as control experiments. As shown in Figure 5a, the MXA–antiperovskite cell with the ether electrolyte displayed stable long-term cyclic performance with a capacity retention of 87.5% up to 400 cycles. The full cell also
maintained high discharge capacities of 144.2 and 123.7 mAh g⁻¹ at the high rates of 2.0 and 5.0 C (1.0 C = 2 mA cm⁻²) with slightly increased voltage polarizations (Figure 5b; Figure S22a, Supporting Information), respectively. On the other hand, the bare lithium cell suffered continuous decrease in discharge capacities during cycling test and significant capacity drops at high rates.

Next, the MXA–antiperovskite cell was evaluated in the commercial carbonate electrolyte with a wide voltage window (2.5–4.2 V vs Li/Li⁺). As shown in Figure 5c, the MXA–antiperovskite cell with 200-µm-thick lithium foil demonstrated a high and cycle-stable full-cell discharge capacity of 142.6 mAh g⁻¹ at 1.0 C, and a small voltage polarization gap of 0.42 V after 50 cycles. In comparison, after 50 cycles, the bare lithium cell with 200-µm-thick lithium foil showed a lower full-cell discharge capacity (113.9 mAh g⁻¹) and a larger polarization gap (0.83 V). In addition, the MXA–antiperovskite cell demonstrated a capacity retention of 86.7% for 300 cycles with high Coulombic efficiencies (>99.5%) (Figure 5d) and showed an ultra-high discharge capacity of 119.7 mAh g⁻¹ at 5.0 C (Figure 5e; Figure S22b, Supporting Information). On the other hand, the discharge capacities of bare lithium cell dropped dramatically with rate increase and eventually failed after 50 cycles at 1.0 C due to the irreversible formation of dead lithium phases and electrolyte depletion.

To further increase the energy density of the full cells with the commercial carbonate electrolyte, the negative-to-positive electrode capacity (N/P) ratio was decreased to 2.0 by reducing the thickness of lithium foil to 20 µm. The MXA–antiperovskite cell with 20-µm-thick lithium foil demonstrated a high full-cell discharge capacity of 142.4 mAh g⁻¹ at the 50th cycle, and the corresponding charge–discharge profile (at 0.5 C 1 mA cm⁻²) is shown in Figure 5f. In addition, the full cell maintained stable cycling performance with high Coulombic efficiencies (>99.5%), showing a capacity retention of 81.5% up to 100 cycles at 0.5 C (Figure 5g). On the other hand, the bare lithium cell with 20-µm-thick lithium foil exhibited a large voltage polarization gap (0.96 V) and a low residual capacity of 101.4 mAh g⁻¹ after 50 cycles. The full-cell performance results verified that the MXA–antiperovskite framework played a critical role in extending the battery’s lifespan under harsh conditions. In addition, the MXA–antiperovskite full cell achieved high energy
density of 415.7 Wh kg{\text{cell}}^{-1} and power density of 231.0 W kg{\text{cell}}^{-1} (based on the active materials in anode and cathode) in comparison with the lithium metal full cells with dual-conductive anodes and cathodes in the literature.\textsuperscript{[5d,9-12,a,b,24a]} Detailed calculations of the full-cell energy and power densities are provided in Table S4, Supporting Information. It is worth noting that our full cell with MXA–antiperovskite anode outperformed the reported lithium metal full cells with carbonate-based electrolyte in terms of energy/power densities (Figure 5h), fulfilling the requirements on high capacity and satisfactory rate performance.

3. Conclusion

In summary, a scalable thermal percolation approach was developed to fabricate a dual-conductive and homogenous MXA–antiperovskite framework for combining the advantages of electronically conductive MXA scaffold and Li_{2}OHCl antiperovskite superionic conductor, as well as overcoming the drawbacks of both. As a result, the MXA–antiperovskite framework achieved two main features that have not been reported before. First, the percolative Li_{2}OHCl antiperovskite phase enabled continuous and extended ionically/ conductive pathways across the electrically conductive MXA scaffold, which dissipated electron fluxes at the scaffold/electrolyte interface during battery-charging and facilitated deep and homogenous lithium deposition within the MXA–antiperovskite framework. Second, as verified by DFT calculations and electrochemical characterizations, the hybridized lithiophilic (MXA)–lithiophobic (antiperovskite) interfaces modulated spatially confined lithium deposition in the MXA–antiperovskite framework, benefiting high-areal-capacities/high-energy-densities and long-term lifespans in the symmetric cells (>1000 h at 4 mAh cm^{-2}) and the full cells (>100 cycles at 415.7 Wh kg{\text{cell}}^{-1}) with MXA–antiperovskite electrodes. The strategy proposed in this work not only benefits the development of dendrite-free lithium metal anodes with high energy/power densities but also provides an alternative approach for constructing dual-conductive host framework with hybridized electron/ion pathways in other emerging battery systems (e.g., zinc metal anode and sulfur cathode).

4. Experimental Section

Synthesis of Ionically Conductive Li_{2}OHCl Antiperovskite: All the chemicals used in this work were used directly without further purification. For the synthesis of Li_{2}OHCl, lithium chloride (LiCl, 99%, Sigma–Aldrich) and lithium hydroxide (LiOH, 99%, Sigma–Aldrich) were mixed thoroughly at a LiCl-to-LiOH molar ratio of 1:1 by using a motor. Then, the mixture was heated at 400 °C in a nickel crucible for 4 h in an argon-filled glovebox. Followed by ball milling at 400 r.p.m. for 10 h, the Li_{2}OHCl crystals with cubic structure were obtained.

Fabrication of Electronically Conductive Ti_{2}C_{2}T_{x} MXene Aerogels (MXAs): Ti_{2}C_{2}T_{x} MXene nanosheet dispersion was prepared by adding 1.0 g of Ti_{3}AlC_{2} MXA powder (Laizhou Kai Ceramic Materials Co., Ltd., China) into the solution containing 1.0 g of lithium fluoride (LiF, 99%, Sigma–Aldrich) and 20 mL of 6.0 M hydrochloric acid (HCl) followed by 24-h stirring at 400 r.p.m. at 35 °C. Afterward, the solid residue was washed with deionized (DI) water until the pH value increased to 7.0. Subsequently, the washed residuals were added to 100 mL of DI water, ultrasonicated for 30 min under N_{2} protection in an ice bath, and then centrifuged at 3500 r.p.m. for 30 min. The supernatant was collected as the final dispersion of Ti_{2}C_{2}T_{x} MXene nanosheets with the concentration of ~5 mg mL^{-1}.

For the preparation of MXAs, 30 mg of thiourea dioxide (99%, Sigma–Aldrich) and 150 µL of ammonia solution (25 wt%) were subsequently added into 5 mL of Ti_{2}C_{2}T_{x} MXene dispersion with a concentration of 5 mg mL^{-1}, where thiourea dioxide was used to prevent the oxidation of MXene nanosheets in alkaline solution. Then, the mixture was sonicated and heated at 90 °C for 4 h. After the solution was cooled to the room temperature, the as-formed MXene hydrogel was rinsed with DI water and ethanol several times to remove the residual impurities. Finally, the MXene hydrogel was freeze-dried for 24 h to get the porous MXAs.

Fabrication of MXA–Only Electrode: The as-synthesized MXA powders were dispersed in N-methyl pyrrolidone (NMP) to form a viscous MXA slurry and then coated on a copper foil followed by drying at 80 °C for 12 h.

Fabrication of Antiperovskite–Only Electrode: Li_{2}OHCl antiperovskite powders were heated at 300 °C on a copper foil on a hotplate, and the molten Li_{2}OHCl was coated on a copper foil by using the doctor-blading method in an argon-filled glovebox.

Fabrication of MXA–Antiperovskite Electrodes (on Copper Foil): Both MXA powders and Li_{2}OHCl antiperovskite crystals were dispersed in NMP at different MXA-to-Li_{2}OHCl mass ratios, and the resulting MXA–antiperovskite slurry was then directly coated on a copper foil followed by drying at 80 °C in an argon-filled glovebox for 12 h. Afterward, the MXA–antiperovskite coated copper foil was heated at 300 °C on a hotplate for 1 h to induce thermal penetration of molten Li_{2}OHCl antiperovskite into MXAs. For the fabrication of dual-conductive MXA–antiperovskite framework with percolative electron/ion pathways, the mass ratio was optimized at MXA-to-Li_{2}OHCl = 2:1.

Fabrication of MXA–Antiperovskite, MXA–Only, and Antiperovskite–Only Electrodes (on Lithium Foil): To transfer the MXA–antiperovskite framework onto a lithium foil, the MXA–antiperovskite framework on a copper foil was assembled face-to-face with a lithium foil and put in between two polyethylene terephthalate (PET) sheets followed by a rolling press, and the MXA–antiperovskite electrode on lithium foil was obtained. The whole transfer process was performed in an argon-filled glovebox at the room temperature. Afterward, the MXA–antiperovskite electrodes (on copper foil and on lithium foil) were punched into the disks (12-mm-diameter) for further usage. The MXA–only and antiperovskite–only electrodes on lithium foils were fabricated with the same approach above.

Fabrication of LiFePO_{4} Cathode: LiFePO_{4}. Super P carbon black, and poly(vinylidene) fluoride (PVdF) were mixed in NMP at a weight ratio of 8:1:1, and the slurry was then vigorously stirred overnight. Afterward, the slurry was coated on an aluminum foil at an areal loading of ~12 mg cm^{-2} (on the basis of LiFePO_{4}) and dried at 80 °C for 12 h. The LiFePO_{4} cathode was punched into the disks (12-mm-diameter) for further usage.

Materials Characterization: X-ray diffraction (XRD) patterns were recorded by an X-ray diffractometer (Bruker, D8 Advance, Cu Kα radiation, λ = 0.154 nm) with a scan rate of 2° min^{-1}. Morphologies and elemental mappings were obtained using a field emission scanning electron microscope (FESEM, FEI Nova NanoSEM 450) operating at 10.0 kV. Morphologies of Ti_{2}C_{2}T_{x} MXene nanosheets were characterized by using a high-resolution transmission electron microscope (HRTEM, JEOL 1010F). Time-of-flight secondary ion mass spectroscopy (ToF SIMS, PHI nano TOF II) combined with ion beam cross-section polisher (CP, GATAN, MODEL 685) was operated to analyze the distribution of lithium deposits across the electrodes. X-ray photoelectron spectra (XPS) were recorded on an X-ray photoelectron spectrometer (Kratos AXIS UltraDLD) via a monochromatic Al X-ray beam (100 µm, 25 W) and equipped with an Au+ sputtering gun, with a photoelectron take-off angle of 90°.

Fabrication and Electrochemical Characterizations of Asymmetric Cells: To evaluate the electrochemical performance of lithium plating/ stripping, an asymmetric cell (CR2032 coin cell) was assembled in an argon-filled glovebox with a Celgard 2400 separator, and the ether electrolyte (1.0 M lithium bis(trifluoromethanesulfonyl)imide [LiTFSI] added into 5 mL of Ti_{2}C_{2}T_{x} MXene dispersion with a concentration of 5 mg mL^{-1}) was used as the electrolyte. The cell was cycled at 0.1 mA cm^{-2} in the voltage range of 0.005–3.0 V vs. Li/Li+. The charge–discharge performance of the cells was investigated using a VMP3 multi-channel electrochemical workstation (Bio-Logic) at a constant current density of 0.1 mA cm^{-2}. The cyclic voltammetry (CV) experiments were carried out using a CHI 760D electrochemical workstation (CH Instruments, USA) at various scan rates between 0.01 and 100 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) measurements were conducted using a VMP3 multi-channel electrochemical workstation (Bio-Logic) in the frequency range of 0.01 Hz to 100 kHz with an amplitude of 10 mV for different states of the cells.
in 1,3-dioxolane [DOL]/1,2-dimethoxyethane [DME] [1:1, v/v] with 10.0 wt% LiNO₃ as the additive or the commercial carbonate electrolyte (1.0 M lithium hexafluorophosphate [LiPF₆] in ethylene carbonate [EC]/dimethyl carbonate [DMC]/diethyl carbonate [DEC], 1:1:1, v/v/v). The MXA–antiperovskite framework (on a copper foil) was used as the working electrode, and a lithium foil was used as the counter electrode. The electrolyte volume was controlled to be 60 µL in each asymmetric cell. Three control experiments, 1) the asymmetric cell composed of a bare copper working electrode and a lithium foil counter electrode, 2) the asymmetric cell composed of an MXA–only working electrode and a lithium foil counter electrode, and 3) the asymmetric cell composed of an antiperovskite–only working electrode and a lithium foil counter electrode, were prepared. For the Coulombic efficiency tests, the asymmetric cells were discharged at two areal capacities of 1 and 4 mAh cm⁻², and the current density was kept at 1 mA cm⁻², followed by charging to 1.0 V (vs Li/Li⁺). Before the Coulombic efficiency tests, all of the asymmetric cells were charged/discharged for several cycles at a current density of 0.1 mA cm⁻² to activate the Li⁺ de-/intercalation processes.

**Fabrication and Electrochemical Characterizations of Symmetric Cells:** To verify the interfacial stability between electrode and electrolyte, a symmetric cell was assembled with a pair of MXA–antiperovskite electrodes (on lithium foil) and the ether liquid electrolyte (or the commercial carbonate electrolyte). The symmetric cells were charged/discharged at two areal capacities of 1 and 4 mAh cm⁻², and the current density was kept at 1 mA cm⁻², followed by charging to 1.0 V (vs Li/Li⁺). Before the Coulombic efficiency tests, all of the asymmetric cells were charged/discharged for several cycles at a current density of 0.1 mA cm⁻² to activate the Li⁺ de-/intercalation processes.

**Fabrication and Electrochemical Characterizations of Full Cells:** For the full-cell fabrication, a coin cell composed of a MXA–antiperovskite anode (on a lithium foil), a LiFePO₄ cathode (12 mg cm⁻² LiFePO₄, 1.0 C = 170 mA g⁻¹), and the ether electrolyte (or the commercial carbonate electrolyte) was fabricated. The electrolyte volume was controlled to be 60 µL in each full cell. As the control experiment, a full cell composed of a bare lithium anode, a LiFePO₄ cathode, and the ether electrolyte (or the commercial carbonate electrolyte) was fabricated. Two kinds of lithium foils with different thicknesses (200- and 20-µm-thick) were used for the fabrication of full cells: the resulting full cells were named as “the MXA–antiperovskite cells”. As control experiments, two types of full cells with bare lithium anodes (200- and 20-µm-thick) were fabricated and named as “the bare lithium cells”. The assembled full cells were tested in a Landt battery test system at the frequency range of 0.1–10⁶ Hz.

**Simulation Methods:** All the density functional theory (DFT) calculations were conducted with the Vienna Ab initio Simulation Package (VASP). The generalized gradient approximation (GGA) and Perdew–Burke–Ernzerhof (PBE) formulations were adopted to describe the exchange correlation energies. The projector augmented wave (PAW) method was used to describe the ionic cores and valence electrons were considered using a plane wave basis with a kinetic energy cutoff of 520 eV[26] Partial occupancies of the Kohn–Sham orbitals were allowed using the Gaussian smearing method with a width of 0.05 eV. The electronic energy was considered to be self-consistent when the energy change was smaller than 10⁻⁶ eV. The convergence criterion of geometry relaxation was set to be smaller than 0.02 eV Å⁻¹ in force. The Brillouin zones (BZ) were sampled by using the surface structures of 11 × 11 × 5 Monkhorst-Pack K point. A vacuum spacing of 18 Å was added along the direction perpendicular to the plane of the slab. To identify the most stable surface model for calculating binding energies, the low Miller-index surfaces of lithium metal (e.g., 001, 110, and 111) and Li₂OHCl (e.g., 100, 010, −100, 110, and 111) were considered. The surface energies were calculated by taking the energy difference between our slab and the same amount of unit cell bulk, which was then divided by the surface area of the slab (including both sides of the slab, Equation (2)).

\[ E_{\text{surf}} = \left( E_{\text{slab}} - nE_{\text{bulk}} \right) / 2S \]

where \( E_{\text{slab}} \) is the total energy of a lithium metal slab units, \( E_{\text{bulk}} \) is the energy of per unit cell bulk of Li₂OHCl or lithium metal, and \( S \) is the surface area of the cleaved plane.

For calculating the binding energies of Li|MxEne|Li and Li|Li₂OHCl|Li interfaces, a four-layer lithium atom was allowed to interact with a 4 × 4 × 1 MXene supercell and a 4 × 4 × 1 Li₂OHCl supercell to build Li|MxEne|Li and Li|Li₂OHCl|Li models, respectively. The Ti₃C₂Tₓ MXene model was built with oxygen terminated groups.[27] The binding energy (\( E_b \)) is defined according to Equation (3),

\[ E_b = E_{\text{total}} - E_{\text{slab 1}} - E_{\text{slab 2}} \]

where \( E_{\text{total}} \) is the total energy of the sandwiched interface model, \( E_{\text{slab 1}} \) and \( E_{\text{slab 2}} \) are the energy of clean slab 1 and slab 2 after relaxation, respectively.

Based on molecular dynamics (AIMD) simulation was carried out to build the Li₂OHCl|MxEne|Li and Li₂OHCl models at 298 K and 600 K. The models at different temperatures were optimized by using a time step of 1 fs in the NVT ensembles together with Nose–Hoover thermostat (20 ps). Finally, the interface models were relaxed with a cutoff energy of 300 eV and a \( 3 \times 3 \times 1 \) Gamma-centered k-mesh.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

This project is supported by the Key Program of the National Natural Science Foundation of China (No. 51732005), Guangdong-Hong Kong-Macao Joint Laboratory (2019B121205001), Guangdong Provincial Key Laboratory (2018B030322001), and the Laboratory for Electrochemical Storage of Energy at AAIS of SUSTech. The authors acknowledge the financial support provided by the Start-Up Fund of University of Maryland, College Park (KFS No.: 2957431 to P.-Y.C.), and Energy Innovation Seed Grant from the Maryland Energy Innovation Institute (MEI^2) (KFS No.: 2957597 to P.-Y.C.).

**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

Research data are not shared.

**Keywords**

Li₂OHCl antiperovskite superionic conductors, lithium metal anodes, percolative electron/ion frameworks, Ti₃C₂Tₓ MXene scaffolds

Received: September 11, 2022
Published online: October 9, 2022
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