Freestanding MXene-MnO$_2$ films for Li-CO$_2$ cathodes with low overpotential and long-term cycling.

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Freestanding MXene–MnO$_2$ Films for Li–CO$_2$ Cathodes with Low Overpotential and Long-Term Cycling

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Abstract

The Li–CO$_2$ battery is a potential energy storage device that not only possesses a theoretical energy density as high as 1876 W h kg$^{-1}$ but also alleviates the consumption of fossil resources by converting the greenhouse gas CO$_2$ into electric energy. However, some technique bottlenecks, such as high overpotential, low recyclability, and low energy density, severely prohibit its application rhythm. Here, we prepare a binder-free MXene–MnO$_2$ composite film using vacuum-assisted filtration and in situ reduction, which can be used as a freestanding cathode for Li–CO$_2$ batteries. This MXene–MnO$_2$ film electrode bestows good cycle stability (∼220 cycles), high specific capacity, and lower overpotential (∼0.89 V) in Li–CO$_2$ batteries. Both experimental tests and first-principles calculations reveal that the enhanced electrochemical properties are associated with three aspects. First, the MXene–MnO$_2$ film offers a high electrical conductivity and porous structure, which provide fast transport channels for electrons and ions. Then, the replacement of Mn by Ti increases the adsorption of Li ions, which facilitates the rapid decomposition of Li$_2$CO$_3$. Finally, the synergistic effect of MXene and MnO$_2$ exposes a large number of active sites, which increases the capacity of Li–CO$_2$ batteries. Therefore, this self-supporting strategy on the MXene composite paves a way to develop high-performance Li–CO$_2$ batteries.

KEYWORDS: Li–CO$_2$ batteries catalyst cycle stability MXene–MnO$_2$ film freestanding cathode

1. Introduction

With increasing demand of high-energy density devices, traditional Li-ion batteries are unable to meet the demands of the transport electrification and large-scale grid energy storage (1–3). Metal–air batteries, due to their unique merits such as high operating voltage and large capacity, have attracted great research attention (4). Among them, Li–CO$_2$ batteries have been considered as a new type of energy storage device, with special interest to reduce CO$_2$ emissions. However, their poor rechargeability and low application current density prohibit the applications. The reversible electrochemical reaction of 4Li + 3CO$_2$ $\leftrightarrow$ 2Li$_2$CO$_3$ + C (E$_0$ = 2.8 V vs Li/Li$^+$) (5,6) can theoretically release a high energy density of 1876 W h kg$^{-1}$ (5,7–9). Metal Li is oxidized at the anode during the discharge process, wherein Li ions are released into the electrolyte, while CO$_2$ gas is reduced at the cathode to...
generate carbonate (CO$_3^{2-}$) anions and amorphous carbon. Therefore, the reversible formation/decomposition of discharge products (Li$_2$CO$_3$) is an important process in Li–CO$_2$ batteries. The discharge product Li$_2$CO$_3$ is a wide-band gap insulator with low conductivity, slow decomposition kinetics, and poor thermodynamic stability, and thus, a high charging voltage is required to completely decompose Li$_2$CO$_3$ during the charging process. However, excessively high overpotential also leads to electrolyte decomposition, which shortens the cycle stability and lifetime of Li–CO$_2$ batteries.

Noble metal-based catalysts have shown low overpotential and high cycling stability, yet the unaffordable cost has hindered their widespread application. Alternatively, transition-metal oxides (TMOs) have gained tremendous attention due to their excellent catalytic properties. For instance, the NiO–CNT composition served as an effective cathode for the Li–CO$_2$ battery with high coulombic stability and good circulation stabilization. The Li–CO$_2$ batteries with ZnCo$_2$O$_4$@CNT cathode exhibited a full load discharge capacity of 4275 mA h g$^{-1}$ and excellent cycling performance. However, some discharge intermediates often result in the premature cell mortality. Moreover, the catalytic performance is also restricted by the high resistance of TMOs. Accordingly, there is an imperative need to develop highly conductive and structure-stabilized TMO-based catalysts.

Figure 1. (a) Schematic diagram of the synthesis of Ti$_3$C$_2$–MnO$_2$ films. Microstructural characteristics: (b) XRD patterns of the Ti$_3$C$_2$ film, MnO$_2$, and Ti$_3$C$_2$–0.1MnO$_2$ film. (c,d) Cross-sectional SEM image of the Ti$_3$C$_2$ film and Ti$_3$C$_2$–0.1MnO$_2$ film. (e) Top-view SEM image of the Ti$_3$C$_2$–0.1MnO$_2$ film. The inset corresponds to its local high-magnification image. (f–i) Corresponding elemental distribution, (j) TEM image, and (k) HRTEM image of the Ti$_3$C$_2$–0.1MnO$_2$ film, respectively.
MXenes are novel two-dimensional nanomaterials derived from a large family of transition-metal carbides, nitrides, and carbon-nitrides and allow for excellent electrical conductivity and efficient charge transportation,\(^{(17)}\) due to abundant exposed metal sites.\(^{(18)}\) These attractive properties make MXenes potential candidates for energy storage and conversion.\(^{(19−25)}\) Notably, MXenes promote rapid electron transfer to electrochemically active sites, facilitating facile electrochemical reactions.\(^{(19)}\) In addition, MXene can also act as a strong support to prevent structural variation during the electrochemical reaction of TMOs.\(^{(26)}\) Among the MXenes, Ti\(_3\)C\(_2\)Tx is particularly notable for high capacitance (≈1500 F cm\(^{-3}\))\(^{(27)}\) in combination with good conductivity (≈15,000 S cm\(^{-1}\)).\(^{(27,28)}\)

Herein, a new flexible, binder-free MXene–MnO\(_2\) combination was prepared as a cathode catalyst for Li–CO\(_2\) batteries by vacuum-assisted filtration and in situ reduction. The synergic effect between MXene and MnO\(_2\) enables the Li–CO\(_2\) battery to perform good cycling stability (≈220 cycles), higher specific capacity, and lower overpotential (≈0.89 V), compared with single MXene film or MnO\(_2\) cathode catalyst. This work paves the way to design a self-supporting cathode catalyst in Li–CO\(_2\) batteries, contributing to the development of high-performance Li–CO\(_2\) batteries.

### 2. Experimental Section

Ti\(_3\)AlC\(_2\) (500 mesh) was bought from Laizhou Kai Kai Ceramic Materials Co., Ltd. LiF (99.99%) was bought from Aladdin Reagent (Shanghai) Co., Ltd., China. Delaminated Ti\(_3\)C\(_2\)Tx suspension was attained via in situ etching Ti\(_3\)AlC\(_2\) powders using LiF/HCl. Specifically, 1.6 g of LiF was added into a Teflon beaker (50 mL) with 20 mL of 9 M HCl under continuous stirring. Then, 1.0 g of Ti\(_3\)AlC\(_2\) powder was slowly added into the mixture solution and maintained at 40 °C for 48 h. The resultant solid residue was washed with deionized water by repeated centrifugation until the pH was above 6. Then, the precipitate was diluted to 200 mL of deionized water and bath sonicated in ice for 1 h. Finally, the solution was centrifuged at 3500 rpm to collect the single or few-layered MXene dispersion. The concentration of this suspension was 2 mg mL\(^{-1}\). Fabrication of Ti\(_3\)C\(_2\)–MnO\(_2\) films: 20 mL of 1.4 mM MnSO\(_4\)·H\(_2\)O was added into 20 mL of the aforementioned MXene suspension and stirred for 1 h. Subsequently, 40 mL of the above-synthesized mixture was prepared using vacuum-assisted filtration through a PVDF membrane. 20 mL of KMnO\(_4\) (1.6 mM) aqueous solution was quickly added into the vacuum-assisted filtration. Finally, the freestanding Ti\(_3\)C\(_2\)–MnO\(_2\) film sediment was stored by freeze drying for 48 h. Different Ti\(_3\)C\(_2\)/MnSO\(_4\) molar ratios of 1:0.05, 1:0.1, and 1:0.2 in the initial solutions were prepared, and the products were designated as the Ti\(_3\)C\(_2\)–0.05MnO\(_2\) film, Ti\(_3\)C\(_2\)–0.1MnO\(_2\) film, and Ti\(_3\)C\(_2\)–0.2MnO\(_2\) film, respectively. The Ti\(_3\)C\(_2\) film and MnO\(_2\) were synthesized in the same way as mentioned above, except that MnO\(_2\) or MXene was not added.

### 2.2. Material Characterization

The crystal structure of the samples was analyzed on an X-ray diffractometer (Rigaku D/Max-2005/PC), which used Cu Ka radiation (λ = 1.5406 Å) with a scan rate of 2°/min. Scanning electron microscopy (SEM) was conducted with a Hitachi S-4800. Transmission electron microscopy (TEM) measurements were taken using a Titan ETEM G2 at 300 kV. The specific surface area and pore size profiles of the samples were investigated by nitrogen adsorption at 77 K (−196 °C) by a Micromeritics ASAP2020. X-ray photoelectron spectroscopy (XPS) illustrations were examined with Al Kα (1486.71 eV) X-ray radiation (15 kV and 10 mA) on a Thermo fisher instrument. The binding energies derived in the XPS analysis were adjusted by referencing the C 1s peak position (284.80 eV).
2.3. Electrochemical Measurements

Due to the low capacity of the Ti$_3$C$_2$ film-based Li–CO$_2$ battery, the electrical current density and specific gravity capacity of all electrodes are derived from the mass of manganese dioxide. The mass loading of the Ti$_3$C$_2$–MnO$_2$ film was found to be 0.5–0.7 mg cm$^{-2}$. The Li–CO$_2$ batteries, based on a CR2032 coin-type battery, were assembled in a glovebox filled with argon with an ambient level of water and oxygen of less than 0.1 ppm. They were made up of a lithium foil anode (14 mm in diam), a glass fiber filter separator (16 mm in diam), an electrolyte (1 M LiTFSI dissolved in TEGDME solution), and an air cathode.

The freestanding Ti$_3$C$_2$–MnO$_2$ film cathodes were cut into disks (12 mm diam). A hole (4 mm in diam) was tapped into the cathode casing so that carbon dioxide could easily and quickly access the cathode. The assembled cell was then kept in a 250 mL glass container fully filled with high purity carbon dioxide. The pure carbon dioxide is pumped into the glass vessel via a direct bi-directional piston, which is alternately evacuated and vented three times. After 10 h incubation, the cells were tested for charge/discharge cycles. For all Li–CO$_2$ cells, 1 M LiTFSI dissolved in TEGDME solution was chosen as the electrolyte. All potentials were compared to Li/Li$^+$. The constant current discharge/charge tests are carried out on the LAND CT2001A battery tester. Cyclic voltammetry (CVs) and electrochemical impedance spectroscopy (EIS) curves were performed at the BioLogic VMP$_3$ system.

2.4. Calculations

In density functional theory (DFT) simulations,$^{29,30}$ the Vienna ab initio Simulation Package (VASP)$^{31}$ was used for geometric optimization and reaction process imitation. Nuclear electrons are denoted by the enhanced wave potential of the emission. We employed generalized gradient approximation with the Perdew–Wang functional (PW91)$^{32}$ to describe exchange and correlation effects. The dynamic power cut-off is 500 eV. The K-point sampling is $7 \times 5 \times 1$. The structure was selected for the
optimization with a force convergence criterion of 0.01 eV/Å and an energy convergence criterion of 10^{-6} eV. The optimized lattice constant of δ-MnO_2 is \(a = b = 0.29\) nm, \(c = 0.51\) nm.

3. Results and Discussion

3.1. Characterization of MXene–MnO_2 Films

A freestanding, binder-free MXene–MnO_2 film is prepared through a vacuum filtering method and redox reaction (precise steps are shown in the experimental section). As depicted in Figure 1a, the Al layers in the pristine bulk Ti_3AlC_2 MAX were selectively removed by etching with mixed LiF/HCl solution. Subsequently, the MXene–MnO_2 film was formed by in situ reduction. The X-ray diffraction (XRD) patterns (Figures 1b and S1a) show that the strong characteristic peak of (002) for the MXene film is moved to a lower angle (2\(\theta = 6.5^\circ\)). Meanwhile, the peak at \(\sim 39^\circ\), corresponding to the (104) plane of Ti_3AlC_2 (SEM Figure S1b), disappeared, which suggests that the Al layers are successfully etched from the MAX phase, and the MXene structure is formed (Figure S2). All peaks in the pattern of MnO_2 are notably indexed to the δ-MnO_2 (JCPDS no. 80-1098), and they remained in the Ti_3C_2–0.1MnO_2 film. The cross-sectional (Figure 1c) and top view (Figure S2b) SEM images of bare Ti_3C_2 film indicate that the well-dispersed few-layer MXene nanosheets can be achieved by simple vacuum filtration. The optical photographs of the curving Ti_3C_2Tx MXene film and the Tyndall effect of laser irradiation (Figure S4a) exhibit excellent flexibility and dispersibility. After vacuum filtration and redox reaction, the MnO_2 nanosheets are uniformly loaded on the Ti_3C_2 film and have a larger specific surface area and better electrical conductivity, as evidenced in Figure 1d (cross-sectional SEM), Figure 1e (top-view SEM), and Figure S4b (optical photographs), compared with separate MnO_2 (Figure S3). The elemental mappings (Figure 1f–i) result with homogeneous C, Ti, O, and Mn distribution in MXene–MnO_2 films, which is also consistent with the easy conglutination between MnO_2 nanosheets and MXene substrates (Figure S5a,b). Additionally, as shown in the high-resolution TEM (HRTEM) image (Figure 1j,k), the lattice spacing of 0.25 and 0.23 nm is assigned to the (200) and (003) planes of the MnO_2, respectively. Finally, the selected area electron diffraction (SAED) pattern (Figure S5c) clearly shows the coexistence of Ti_3C_2 films and MnO_2 nanosheets. As a comparison, different concentrations of MnO_2 grown in situ on MXene were prepared, and they are termed as Ti_3C_2–0.05MnO_2 and Ti_3C_2–0.2MnO_2 films, respectively. The morphology of MnO_2 varies depending on the concentration, as shown in Figures S6 and S7.

In addition, as assessed by XPS (Figure 2a), the characteristic peaks of Ti 2p, O 1s, C 1s, F 1s, and Mn 2p are observed, indicating the appearance of these ingredients in the combination. In the Mn 2p fine spectrum (Figure 2b), the splitting energy from the Mn 2p of MnO_2 to that of the Ti_3C_2–0.1MnO_2 film is 11.8 eV. Moreover, the overall binding energy of the Ti_3C_2–0.1MnO_2 film shifts to a lower binding energy, owing to electron transfer between the functional groups of the MXene surface and MnO_2. On the other hand, since Ti occupies the active site of Mn, the O 1s fine spectrum of the Ti_3C_2–0.1MnO_2 film (Figure 2c) moves slightly to the direction of high binding energy. Consistently, the Ti 2p fine spectra have almost unchanged before and after reaction (Figure 2d). This phenomenon has occurred in our previous work. The variation of specific surface area and pore size is further investigated by the Brunauer–Emmett–Teller (BET) test. Basically, compared with the pristine Ti_3C_2 film (9.07 m²/g), the formed Ti_3C_2–0.1MnO_2 film composite material sample has the larger BET surface area of 14.55 m²/g (Figure 2e), offering more active sites for CO_2 in the charging and discharging processes than other counterparts. More importantly, the Ti_3C_2–0.1MnO_2 film has larger coarse pores which facilitate ion and electron transportation, as shown in Figure 2f.
3.2. Electrochemical Properties

CV curves were determined at a scan rate of 0.2 mV s\(^{-1}\) with Li/Li\(^+\) in the range of 2–4.5 V at high purity CO\(_2\) (Figure 3a). Compared with those of the pure MnO\(_2\) cathode, the Ti\(_3\)C\(_2\)–0.1MnO\(_2\) film cathode performs a higher CO\(_2\) reduction reaction onset potential (CO\(_2\)RR, \(\approx 2.36\) V) and a lower CO\(_2\) evolution reaction onset potential (CO\(_2\)ER, \(\approx 3.8\) V).\(^{(5)}\) The results show that the Ti\(_3\)C\(_2\)–0.1MnO\(_2\) film electrode is beneficial for both the formation and decomposition of Li\(_2\)CO\(_3\) in Li–CO\(_2\) batteries. Figure 3b shows the voltage distribution of the flexible, binder-free Ti\(_3\)C\(_2\)–0.1MnO\(_2\) film cathode in Li–CO\(_2\) batteries at different current densities. Under CO\(_2\) conditions, the batteries have a capacity of 5722, 2525, and 1007 mA h g\(^{-1}\) at current densities of 100, 200, and 500 mA g\(^{-1}\), respectively. When the
discharge/charge capacity is limited to 1000 mA h g⁻¹ at a current density of 100 mA g⁻¹, as shown in Figure 3c, the Ti₃C₂–0.1MnO₂ film cathode exhibits low polarization with a discharge overcharge potential of 0.89 V in the tenth cycle. On the contrary, the overpotential adds up to 1.33 V for the Ti₃C₂ film and 1.87 V for MnO₂, respectively. The cycling performance of the Ti₃C₂–0.1MnO₂ film electrode was examined to evaluate its electrocatalytic activity and stability. Figure 3d shows that the Li–CO₂ batteries with Ti₃C₂–0.1MnO₂ film electrode exhibit stable and reversible cycling over 220 cycles at 100 mA g⁻¹. They are able to withstand 180 (Figure S8a,b) and 60 (Figure S8d,e) cycles when the electrical current density is 200 and 500 mA g⁻¹, respectively. Furthermore, the Ti₃C₂–0.05MnO₂ film, Ti₃C₂–0.2MnO₂ film, pure MXene film, and MnO₂ electrode were also tested under the same conditions, and they only show 50 (Figure S9a,b), 60 (Figure S9d,e), 30 (Figure S10a,b), and 20 (Figure S11a,b) cycles, respectively, which demonstrates the best catalytic activity and cycling stability than that of the Ti₃C₂–0.1MnO₂ film. Moreover, the Ti₃C₂–0.1MnO₂ film cathode delivers a higher discharge capacity at 100 mA g⁻¹, while those of MnO₂-based cathodes are only 2757 mA h g⁻¹ (Figure 3e). As summarized in Figure 3f, the recycling behavior of Li–CO₂ batteries with the Ti₃C₂–0.1MnO₂ film cathode is the best among the Mn oxide-based materials, as cathodes for Li–CO₂ battery literature surveyed (36–44). In addition, the specific capacities of the first five turns of the Ti₃C₂–0.1MnO₂ film cathode catalyst for current densities of 200 and 500 mA g⁻¹ are shown in Figure S8c,f, respectively. Figure 3g presents the cycling galvanostatic discharge/recharge curves of the hybrid Ti₃C₂–0.1MnO₂ film cathode with the fixed capacity of 1000 mA h g⁻¹ at a current density of 100 mA g⁻¹, and it maintains a stable terminal discharge voltage above 2.0 V after 220 cycles. Furthermore, a concrete comparison of the cycle numbers for the five different sample-equipped electrodes in Li–CO₂ batteries is shown in Figure S12.
3.3. Reaction Mechanism

Figure 4a shows preliminary circular electrostatic discharging/charging characteristic with the Ti$_3$C$_2$–0.1MnO$_2$ film as the cathode at a current density of 100 mA g$^{-1}$. As shown in Figure 4b, the typical peaks of Li$_2$CO$_3$ (JCPDS no. 22-1141) can be easily detected in the discharging Li–CO$_2$ battery with the Ti$_3$C$_2$–0.1MnO$_2$ film cathode. However, after charging, the characteristic peak of Li$_2$CO$_3$ disappears, suggesting the complete decomposition of the discharge product. In addition, the reversible formation/decomposition of Li$_2$CO$_3$ is further verified by Fourier-transform infrared (Figure S13). Figure 4c shows the EIS spectrum of the Ti$_3$C$_2$–0.1MnO$_2$ film electrode during the charging and discharging cycles at 100 mA g$^{-1}$. Compared with the pristine electrode, a larger semicircle appears in the discharged state, indicating that the precipitation of the insulating discharging product Li$_2$CO$_3$ on the surface of the Ti$_3$C$_2$–0.1MnO$_2$ film electrode leads to a significant increase in impedance. However, the pristine interface (high-frequency part), charge transfer (high-middle frequency region), and diffusion resistance (straight line) can be recovered to a large extent during the subsequent charging process. EIS plots (Figure S14a–d) and fitting parameters of EIS curves (Tables S1–S3) uncover that
Ti3C2–0.1MnO2 film has the smallest value of surface film resistance (Rf) and charge-transfer resistance (Rct) among the samples considered, proving its good conductivity at the same time.

XPS spectrum of Li 1s (Figure 4d) for the discharged Ti3C2–0.1MnO2 film shows a characteristic peak at 55.2 eV, assigned to Li2CO3, which then disappears after the full recharge process, verifying the complete decomposition of Li2CO3 and the high reversibility of the Li–CO2 battery. The fine spectrum of Mn 2p (Figure 4e) shows that the binding energy of Mn 2p is maintained during the charging and discharging process, which demonstrates the superior stability of the Ti3C2–0.1MnO2 film during the cycle of the Li–CO2 cell. Interestingly, the fine spectrum of Ti 2p (Figure 4f) during the charge/recharge process changes a little, which might be associated with electron transfer from Ti to Mn. The SEM image shows that the surface of pristine Ti3C2–0.1MnO2 film is smooth and clean (Figure 4g). However, the discharge product Li2CO3, like a paste, is uniformly deposited on the catalyst surface after discharging (Figures 4h and S15a). Moreover, the surface morphology of the cathode catalyst returns to its original state (Figures 4i and S15b,c), which demonstrates the good reversibility and stability of the Ti3C2–0.1MnO2 film as a catalyst.

To clarify the mechanism of the electrocatalytic activity of the Ti3C2–0.1MnO2 film cathode, DFT calculations have been performed. Crystal texture and band structures of δ-MnO2 and MXene/δ-MnO2 are shown in Figures 5a and S16. According to the structure, the MnO2 lamellar gap is a tetrahedral gap, which becomes an octahedral gap in MXene/δ-MnO2 after in situ growth on MXene. Simultaneously, the H atoms in the functional group of MXene combine with the O atoms in MnO2. Moreover, Figure 5b discloses that the adsorption energy of lithium in MXene/δ-MnO2 is the highest. As shown in the band structure, MnO2 is a wide band gap semiconductor with poor electrical conductivity, but after the H–O bonding, it becomes a conductor with significantly increased electron population on the Fermi level, as depicted in the density of states (DOS) (Figure 5c,d). Specifically, the main contribution to the Fermi energy level is from the Ti 3d orbital, which enhances the
electrocatalytic activity of the cathode by replacing the sites of Ti. Additionally, as shown in Figure S17a, in the model wherein one of the Mn is replaced by Ti in MnO₂, the bond length of Mn–O is shorter than that of the Ti–O bond, which is due to the fact that the electronegativity of Ti is not as large as that of Mn. After the substitution, the adsorption energy is enhanced for TiₓMn₁₋ₓO₂, which promotes the reaction between CO₂ and Li to form Li₂CO₃. The adsorption energies of different Li with the three cases are shown in Figure S17b, among which the adsorption energy of TiₓMn₁₋ₓO₂ is the largest.

4. Conclusions

The stand-alone and binder-free MXene–MnO₂ composite electrode in the field of Li–air batteries was synthesized by vacuum filtration and redox reaction. Based on this self-supporting cathode catalyst, the Ti₃C₂₋₀.₁MnO₂ film-based Li–CO₂ cell can be stably cycled (220 cycles) at a lower overpotential even when operating at a fixed capacity of 1000 mA h g⁻¹ at 100 mA g⁻¹. After the pre-activation process, the overpotential of the charge/discharge curve was as low as 0.89 V at the tenth cycle compared with the Ti₃C₂ film and MnO₂ cathode. The excellent electrocatalytic activity performance can be ascribed to the following reasons. First, the high electrical conductivity and porous structure of the MXene–MnO₂ film provide fast electron and ion transport channels during the charging and discharging process. Second, the replacement of Mn by Ti increases the adsorption of lithium ions and facilitates the rapid decomposition of Li₂CO₃. Third, the synergistic effect between the MXene film and MnO₂ exposes more active sites, which in turn increases the capacity of the Li–CO₂ batteries. The pioneering effort of this study is to investigate MXene as a freestanding catalyst for catalytic activity enhancement and discharge product control in Li–CO₂ batteries, which provides a new perspective on the design of catalysts for rechargeable metal-gas batteries.

Notes

The authors declare no competing financial interest.

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Supporting Information

Freestanding MXene-MnO$_2$ Films for Li-CO$_2$ Cathodes with Low Overpotential and Long-term Cycling

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AB107GJ, United Kingdom
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<th>Samples</th>
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<th>$R_e$ (Ω)</th>
<th>$R_f$ (Ω)</th>
<th>$Q_1$</th>
<th>$R_{ct}$ (Ω)</th>
<th>$Q_2$</th>
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<td>336.1</td>
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Table S2. Fitting parameters of EIS curves of the Ti$_3$C$_2$-0.2MnO$_2$ film sample in terms of fitting circuits.

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<th>$R_f$ (Ω)</th>
<th>$Q1$ Y</th>
<th>$R_{ct}$ (Ω)</th>
<th>$Q2$ Y</th>
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Table S3. Fitting parameters of EIS curves of the Ti$_3$C$_2$-0.1MnO$_2$ film, Ti$_3$C$_2$ film and MnO$_2$ sample in terms of fitting circuits, respectively.

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<th>Samples</th>
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<th>$R_e$ (Ω)</th>
<th>$R_f$ (Ω)</th>
<th>$Q_1$</th>
<th>$R_{ct}$ (Ω)</th>
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Figure S1. a) XRD pattern and b) SEM image of the MAX phase Ti$_3$AlC$_2$. 
Figure S2. a) TEM image of MXene nanosheets. The inset is the selected area electron diffraction pattern of MXene. b) Top-view SEM image of Ti$_3$C$_2$ film.
Figure S3. a) SEM image of MnO$_2$. The inset corresponds to its local high-magnification image.
Figure S4. a) Optical photographs of curving MXene film. The inset is tyndall effect of laser irradiation. b) Optical photographs of Ti$_3$C$_2$-0.1MnO$_2$ film.
Figure S5. a-b) TEM, and c) the selected area electron diffraction pattern of Ti$_3$C$_2$-0.1MnO$_2$ film, respectively.
Figure S6. a) XRD pattern and b) SEM, c) TEM, d) HRTEM image of Ti$_3$C$_2$-0.05MnO$_2$ film respectively. The inset of b) is local high-magnification image of Ti$_3$C$_2$-0.05MnO$_2$ film.
Figure S7. a) XRD pattern and b) SEM, c) TEM, d) HRTEM image of Ti$_3$C$_2$-0.2MnO$_2$ film respectively. The inset of b) is local high-magnification image of Ti$_3$C$_2$-0.2MnO$_2$ film.
Figure S8. a) Discharge-charge cycling stability of Ti$_3$C$_2$-0.1MnO$_2$ film at 200 mA g$^{-1}$ with a cut-off capacity of 1000 mA h g$^{-1}$. b) Cycling stability and terminal discharge-charge voltages of Ti$_3$C$_2$-0.1MnO$_2$ film cathode at 200 mA g$^{-1}$ with a limited capacity of 1000 mA h g$^{-1}$. c) The first charge/discharge properties of Ti$_3$C$_2$-0.1MnO$_2$ film under 200 mA g$^{-1}$. d) Discharge-charge cycling stability of Ti$_3$C$_2$-0.1MnO$_2$ film at 500 mA g$^{-1}$ with a cut-off capacity of 1000 mA h g$^{-1}$. e) Cycling stability and terminal discharge-charge voltages of Ti$_3$C$_2$-0.1MnO$_2$ film cathode at 500 mA g$^{-1}$ with a limited capacity of 1000 mA h g$^{-1}$. f) The first charge/discharge properties of Ti$_3$C$_2$-0.1MnO$_2$ film under 500 mA g$^{-1}$. 
Figure S9. a) Discharge-charge cycling stability of Ti$_3$C$_2$-0.05MnO$_2$ film at 100 mA g$^{-1}$ with a cut-off capacity of 1000 mA h g$^{-1}$. b) Cycling stability and terminal discharge-charge voltages of Ti$_3$C$_2$-0.05MnO$_2$ film cathode at 100 mA g$^{-1}$ with a limited capacity of 1000 mA h g$^{-1}$. c) The first charge/discharge properties of Ti$_3$C$_2$-0.05MnO$_2$ film under 100 mA g$^{-1}$. d) Discharge-charge cycling stability of Ti$_3$C$_2$-0.2MnO$_2$ film at 100 mA g$^{-1}$ with a cut-off capacity of 1000 mA h g$^{-1}$. e) Cycling stability and terminal discharge-charge voltages of Ti$_3$C$_2$-0.2MnO$_2$ film cathode at 100 mA g$^{-1}$ with a limited capacity of 1000 mA h g$^{-1}$. f) The first charge/discharge properties of Ti$_3$C$_2$-0.2MnO$_2$ film under 100 mA g$^{-1}$. 

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Figure S10. a) Discharge-charge cycling stability of Ti$_3$C$_2$ film at 100 mA g$^{-1}$ with a cut-off capacity of 1000 mA h g$^{-1}$. b) Cycling stability and terminal discharge-charge voltages of Ti$_3$C$_2$ film cathode at 100 mA g$^{-1}$ with a limited capacity of 1000 mA h g$^{-1}$. c) The first charge/discharge properties of Ti$_3$C$_2$ film under 100 mA g$^{-1}$. 
Figure S11. a) Discharge-charge cycling stability of MnO$_2$ at 100 mA g$^{-1}$ with a cut-off capacity of 1000 mA h g$^{-1}$. b) Cycling stability and terminal discharge-charge voltages of MnO$_2$ cathode at 100 mA g$^{-1}$ with a limited capacity of 1000 mA h g$^{-1}$. c) The first charge/discharge properties of MnO$_2$ under 100 mA g$^{-1}$. 
Figure S12. The cycle numbers of Li-CO\textsubscript{2} batteries with different samples.
Figure S13. FTIR of the MXene-MnO$_2$ film electrodes at different states.
Figure S14. The electrochemical impedance spectroscopy (EIS) determined the impedance of the battery under three states of electrodes with a) Ti$_3$C$_2$-0.05MnO$_2$ film, b) Ti$_3$C$_2$-0.2MnO$_2$ film, c) Ti$_3$C$_2$ film, d) MnO$_2$ respectively.
Figure S15. SEM images of the Ti$_5$C$_2$-0.1MnO$_2$ film based cathode in different: top-view SEM (a) 30$^{\text{th}}$ discharge, (b) 30$^{\text{th}}$ recharge, (c) cross-sectional SEM 30$^{\text{th}}$ recharge.
Figure S16. Band structures of $\delta$-MnO$_2$ a) and MXene/$\delta$-MnO$_2$ b), respectively.
Figure S17 a) Schematic model for adsorption of lithium in a) MnO$_2$, Ti$_x$Mn$_{1-x}$O$_2$, respectively. b) The adsorption energy of lithium in Ti$_3$C$_2$, MnO$_2$, Ti$_3$C$_2$O$_2$ (001), Ti$_x$Mn$_{1-x}$O$_2$, respectively.