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Capacitance changes associated with cation-transport in free-standing flexible $Ti_3C_2T_x$ (T=O, F, OH) MXene film electrodes

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ABSTRACT

Free-standing $Ti_3C_2T_x$ MXene films with flexible feature are considered to be promising electrodes for the application in flexible energy devices. Exploring the different cation effect and each transport mechanism will help us to identify the optimized cation for special applications. Herein, we investigate the relationship between cation transports and capacitance behavior under different potential windows. In addition, we uncover intercalation mechanisms for Li^+, Na^+, and K^+-containing electrolytes. As a result, we found that capacitive intercalation mechanism of characteristic cation can be influenced by different potential windows. Importantly, after 5000 charge-discharge cycles from −1 V to 0 V, the cation-intercalation behavior is demonstrated by significant electrode expansion in LiCl, NaCl, and KCl electrolytes with the increased d-spacing of 1.344 nm, 1.313 nm, and 1.305 nm, respectively. Additionally, larger size of K^+ with fast ion transport is involved in fast electrochemical surface adsorptions, which explains higher capacitance of 346 F cm^{-3} in KCl than 218 F cm^{-3} in NaCl electrolyte. In contrast, small ion size of Li^+ is vulnerable to adsorb and permeate the spacing between layers of $Ti_3C_2T_x$ MXene electrode, which delivers volumetric capacitance of 320 F cm^{-3}. The present study provides direct experimental evidence for electrochemical mechanism of cation intercalation between $Ti_3C_2T_x$ MXene layer sheets.

1. Introduction

The free-standing conductive film is emerging as an attractive alternative electrode for flexible energy storage devices [1], due to its excellent electrochemical performance and easy fabrication [2]. There are two types of free-standing electrodes in categories. One encompasses paper-supported electrodes and the other includes paper-like electrodes that involve graphene-based, CNT-based, carbon-fiber based, and carbon-free based electrodes [3]. The free-standing carbon-free electrode, such as MoS_2 [4], MoO_3 [5], and MnO_2 [6], in comparison with other options, is able to offer high capacitance for a supercapacitor. However, poor electronic conductivity and structural instability in these electrodes are still two obstacles that researchers must overcome. Alternatively, MXene (denoted as $M_{n+1}X_nT_x$, where M is early transition metal, X is C and/or N, and T is terminal group) has the noticeable advantage of great electronic conductivity and chemical stability, which provides particularly high energy-storage capacity [7]. The $Ti_3C_2T_x$ as one representative of MXene has been extensively studied because of its low formation energy [8]. The fundamental research on the free-standing $Ti_3C_2T_x$ electrodes, however, is still in preliminary stages, especially for the electrochemical characteristics on the basis of different potential windows and electrolytes.

Several electrolytes have been considered to be used for the free-standing $Ti_3C_2T_x$ supercapacitor electrode, of which intercalation behaviors are reported under different potential windows. Summarizing the potential windows in the previous reports with different electrolytes, it was −0.3 V–0.2 V for H_2SO_4 electrolytes [8], −0.95 V ~ −0.4 V for alkaline KOH electrolytes [9], and −0.6 V–0.2 V for neutral KCl electrolytes [10]. Even extending to organic and ionic-liquid electrolytes of 1-ethyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)-imide (EMITSI)/acetonitrile, the $Ti_3C_2T_x$ electrode has been proved to present redox peaks under broader potential window from −0.8 V to 1.0 V [11]. All above electrolytes are involved in getting insight into inner electrochemical mechanisms including intercalations and redox reactions.

Nevertheless, the efforts to replace the aqueous electrolyte to the advanced organic electrolyte for extending potential window have been limited, especially because of the presence of low

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gravimetric and volumetric capacitance [12,13]. This limitation of capacitance enhancement is mainly due to larger cation size, lower ionic conductivity and solvation energy, and even the loss of proton-induced pseudo-capacitance [14]. Exploring ideal ionic and/or solvated cation size of aqueous electrolytes is essential for capacitance enhancement in $Ti_3C_2T_x$ electrodes. In particular, alkali metal-based Li^+, Na^+, and K^+ electrolytes play a significant role in intercalation-based energy storage. Through electrochemical quartz-crystal admittance and *in-situ* electronic conductance, capacitive paradox and significant deformation response of $Ti_3C_2T_x$ electrode have been reported during electrochemical intercalation of various cations [10]. Under different potential windows, however, the capacitance and electrochemical characteristics of $Ti_3C_2T_x$ film electrodes associated with each cation transport have not been systematically evaluated in detail. Moreover, below the potential of −1 V after 5000 long-time charge-discharge cycling, the appearance of increase in the cation-intercalation capacitance along with the shrinkage or expansion of lattice spacing in MXene electrode has not been explained clear.

Herein, we performed an extensive study on the effect of potential windows on capacitance and electrochemical intercalation mechanism in free-standing flexible $Ti_3C_2T_x$ film electrode during the cation intercalations of Li^+, Na^+, and K^+-containing electrolytes. We found that typical redox reaction and characteristic capacitive intercalations were presented under potential windows from −0.6 V to 0.4 V and −1 V to 0 V, respectively. Poor ion transport in the NaCl electrolyte restricted the electrode capacitance and exhibited the lowest volumetric intercalation capacitance as compared to LiCl and KCl electrolytes. Additionally, after 5000 charge-discharge cycles at high current density, a mechanism that can be responsible for offering high capacitance of the electrodes in Li^+ and K^+-containing electrolytes was proposed, which provides deep insight into electrochemical mechanism of free-standing $Ti_3C_2T_x$ film electrode.

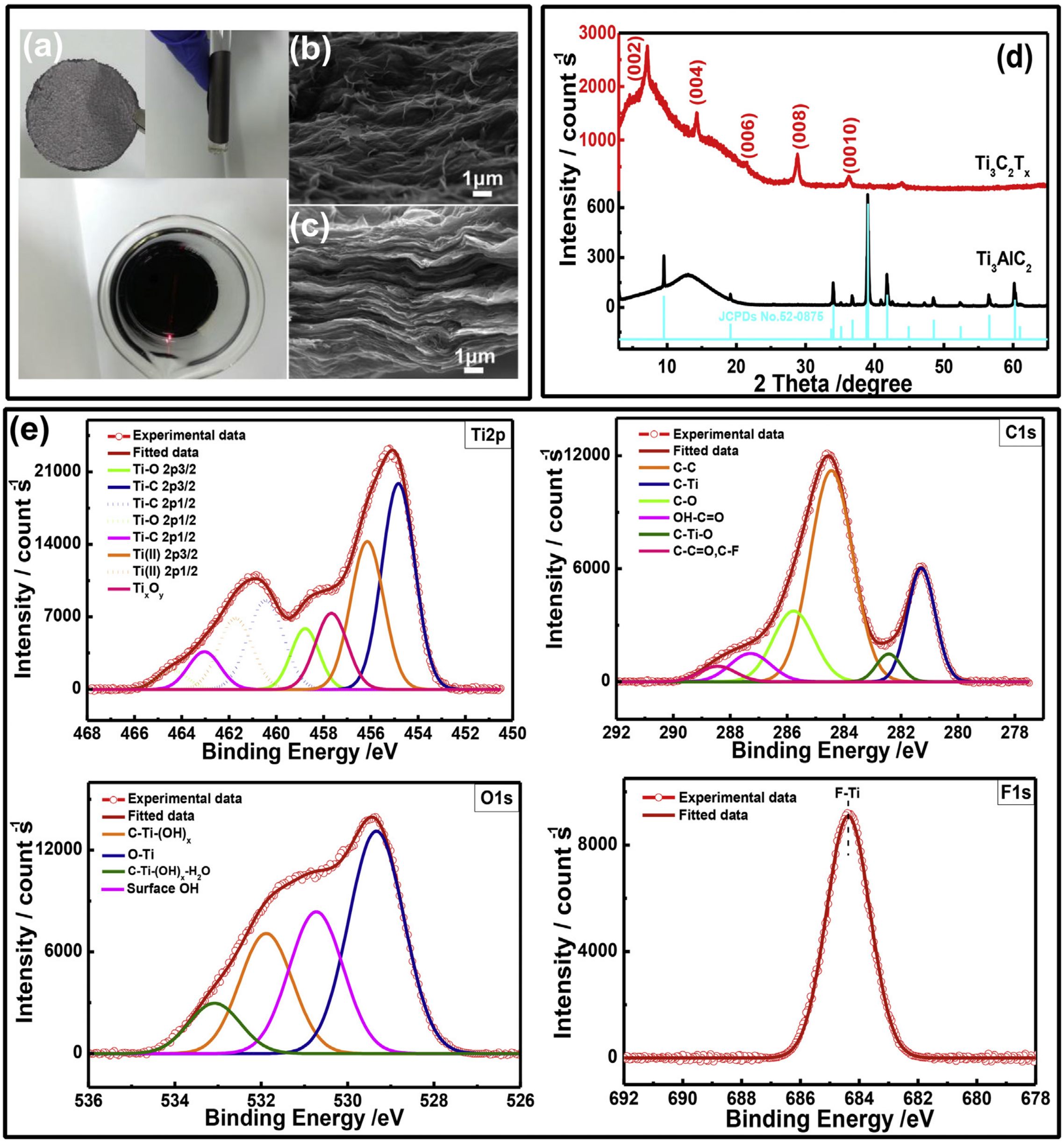

Fig. 1. Characterization of the free-standing $Ti_3C_2T_x$ film. (a) Photographs, (b) Top-view and (c) Cross-section SEM images, (d) XRD patterns, and (e) High-resolution XPS spectra of Ti 2p, C 1s, O 1s, and F 1s.