Synergetic effects of K^+ and Mg^{2+} ions intercalation on electrochemical and actuation properties of two-dimensional Ti_3C_2 MXene

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Abstract

Two-dimensional materials, such as MXenes, are attractive candidates for energy storage and electrochemical actuators due to their high volume changes upon ion intercalation. Of special interest to boost energy storage is the intercalation of multivalent ions such as Mg^{2+} which suffers from sluggish intercalation and transport kinetics due to its ion size. By combining traditional electrochemical characterization techniques with electrochemical dilatometry and contact resonance atomic force microscopy, the synergetic effects of pre-intercalation of K^+ ions are demonstrated to improve charge storage of multivalent ions, as well as tune mechanical and actuation properties of Ti_3C_2 MXene. Our results have important implications for quantitatively understanding the charge storage processes in intercalation compounds and provide a new path for studying the mechanical evolution of energy storage materials.

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Introduction

Electricity generated from intermittent and renewable energy sources, such as wind and solar, requires reliable and sustainable energy storage devices. In the past decades, electrochemical capacitors (supercapacitors) have drawn considerable attention for applications in portable electronics, grid and transportation systems due to their rapid power delivery and an almost unlimited cycle life.[1] The charging that takes from seconds to minutes ensures fast energy harvesting, but supercapacitors store 1-2 orders of magnitude less energy than most batteries.[2] Consequently, the global efforts focuses on enhancing the energy density without sacrificing the power density and cycling stability. To achieve this goal, new electrode materials and electrolytes, and novel electrochemical concepts must be explored.[3]

In search for new materials, two dimensional (2D) transition metal carbides – MXenes, are of particular interest owing to their excellent electrical conductivity and high volumetric capacitance.[4, 5] A variety of aqueous cations can be electrochemically intercalated into Ti_3C_2, the most studied MXene to date, resulting in very high volumetric capacitance outperforming a variety of carbons.[5, 6] The mechanism for high capacitance was essentially described as intercalation pseudo-capacitance arising from redox reactions of the Ti atoms.[7] On the other hand, Ti_3C_2 shows intercalation capacitive behavior even at quite high rates, while normally a slow intercalation takes place in layered battery materials.

Similar to graphite or other electrode materials in various electrolytes,[8-12] MXene electrodes also show a significant change in sample volume when ions are intercalated. This was demonstrated by a range of techniques including electrochemical quartz-crystal admittance (EQCA),[13] *in situ* X-ray diffraction (XRD),[5, 13-16] electrochemical dilatometry (ED), and atomic force microscopy (AFM).[17] These studies revealed that MXene expands or contracts depending on the ion charge to size ratio and that the achieved material strains are large enough to make this material an attractive candidate for electrochemical actuators with good tunability. Therefore, it is of fundamental interest to investigate and understand changes in mechanical behavior of electrodes upon ions intercalation and their spatial variation to evaluate new functionalities or possible lifetime limiting behavior.

The strong correlation between ion intercalation and mechanical properties, such as electrode volume or Young's modulus E, can also be used to employ new characterization techniques to visualize the ion mobility in electrode materials or intercalation pathways. Atomic force microscopy has become a key tool to reveal nano-mechanical properties with a high z (height) resolution below 1 nm and lateral resolution of ~ 20 nm (limited by the tip geometry).[18, 19] This technique is capable of studying thin or film electrodes, extracting ion insertion kinetics in a spatially resolved manner, and is important for building structure-function relationships. This technique has been successfully used to investigate the dimensional variations of lithium ion battery, [20-22] pseudo-capacitors, [23, 24] and electric double layer capacitors.[11, 12]

Amongst numerous dynamic AFM methods, contact resonance (CR) AFM is the most promising for the quantitative characterization of the elasticity of materials with high spatial resolution. To date, CR-AFM has rarely been employed in aqueous media due to difficulties with obtaining clean contact cantilever transfer functions in liquids.[25] Recently, the "*BlueDrive™*" photothermal excitation has reinvented the tapping mode AFM with remarkably simple, stable, and clean response enabling quantitative imaging in liquids.[25] In particular, the recently developed and commercialized band excitation (BE) method extended the capabilities of traditional single-frequency AFM and allowed efficient decoupling between instrumental parameters, direct and indirect topographic cross-talk, and intrinsic material functionality.[26] A combination of "*BlueDrive*^{TM}" and BE methods offers a universal approach for CR-AFM to determine not only structure, but also map Young's modulus of materials at the nanoscale. In our previous work, *in situ* CR-AFM was employed to explore Young's modulus of Ti_3C_2 electrodes during electrochemical intercalation of cation in aqueous media.[17, 24] Changes in Young's modulus were compared with the electrode morphology and electrochemical dilatometry results, and it was found that Li^+ insertion leads to a contraction of the electrode and that there are preferred ion intercalation pathways, as shown by the local increase in Young's modulus. At the same time, K^+ insertion does not lead to any significant electrode volume changes and no change in Young's modulus upon electrochemical cycling. This could be explained by the difference in solvation shells when entering the interlayer space in the MXene electrode.[13] A more recent work reports the intercalation of K^+ resulting in a MXene with uniform, homogenous structure and improved stability of this 2D material against the changes of working environment.[27]

In order to improve the amount of stored charge in electrochemical capacitors, the intercalation of multivalent ions is of special interest. In the case of MXene, Mg^{2+} has been studied the most.[5, 13, 17, 28] In this work, we explore if the above mentioned advantages of K^+ insertion can be coupled with Mg^{2+} intercalation to improve charge storage in Ti_3C_2 MXene. Of interest is the role of pre-intercalation in electrochemical performance and changes in mechanical and actuation properties. We demonstrate the synergetic effects of cations for Ti_3C_2 electrodes through traditional cyclic voltammetry (CV) and, for the elastic properties, through *in situ* CR-AFM complemented by electrochemical dilatometry. The goal is to achieve a fundamental understanding of the interplay between intercalated cations and the electrochemical behavior and mechanics of MXenes.

Experimental

$Ti_3C_2T_x$ (T_x stands for the mixed surface terminations O, OH, and F) was synthesized by etching Al from Ti_3AlC_2 using 48% concentrated hydrofluoric acid (HF) at room temperature (RT) for 18 h as described elsewhere.[5] After washing to remove the etching products followed by drying, $Ti_3C_2T_x$ powder was intercalated by dimethylsulfoxide (DMSO). Then, the intercalated MXene was sonicated in deionized water and centrifuged. The resulted colloidal solution of delaminated MXene was vacuum-filtered to produce free-standing MXene "paper" with the thickness of 2 μm. [5] The latter, consisting of parallel flakes aligned in-plane, was used directly as the working electrode.

Electrochemical cycling was done in 1 M $MgSO_4$ or 0.5 M K_2SO_4 until a steady state was reached. To investigate the effects of K^+ pre-intercalation, cycling was first done by using 0.5 M K_2SO_4 and then continued with 1 M $MgSO_4$ after the electrolyte in the respective electrochemical cell was completely exchanged. In between the electrolyte exchange, the cell was carefully rinsed with Millipore Milli-Q water (18 MΩ cm).

CR measurements were conducted on a Cypher AFM (Oxford Instruments, UK) in air and liquid environments using the BE approach during scanning in contact mode.[26] A 120 kHz large frequency excitation band was sent to the cantilever by a "*BlueDrive^{TM}*" photothermal laser at the base of the cantilever. The cantilever response was detected and then Fourier transformed to extract the contact resonance peak. The contact resonance frequency was extracted from each contact resonance curve via fitting using a simple harmonic oscillator (SHO) model. Tip calibrations were conducted in air and in 18 MΩ deionized water on reference samples (freshly cleaved HOPG and fused silica obtained from Bruker, Germany). The respective Young's moduli were 18 GPa for HOPG and 72.9 GPa for fused silica. The tip used in this study was a gold-coated silicon probe (PPPFM-Au, Nanosensors, USA) with a spring constant $k_c \sim 2$ N/m and a free resonance frequency in air $f_0 \sim 65$ kHz. Typical parameters for the cantilever employed were: $L = 225$ μm, $L_1 = 215$ μm, $h = 12$ μm, and angle = 12°. The procedure for the extraction of Young's modulus from the contact resonance maps has been described elsewhere[24]. All measurements were performed in a three-electrode cell in a stainless steel container, which was attached to the scanner and contained an activated carbon (AC) counter electrode (YP50F, Kuraray, Japan), a Pt wire quasi-reference electrode (0.2 V *vs.* Ag/AgCl) and a 3×3 mm^2 MXene paper working electrode in a lateral arrangement for easy access of the AFM tip to the working electrode. The activated carbon counter electrode was made by mixing AC with PTFE binder (Sigma-Aldrich, USA). The cell was connected to a potentiostat (VSP 200, Biologic S.A., France) for controlling the state of charge of the MXene. In all experiments, the AFM scan rate was kept constant at 1 μm s^{-1} with the scanned area of 2×2 μm^2. CR-AFM measurements were performed after 25 cycles of cyclic voltammetry from -0.2 V to -0.8 V *vs.* Pt wire quasi-reference electrode (0.2 V *vs.* Ag/AgCl) at 5 mV s^{-1} in aqueous 1 M $MgSO_4$ (Sigma Aldrich, USA) without and with previous cycling in 0.5 M K_2SO_4 (Sigma Aldrich, USA), to investigate the effect of K^+ pre-intercalation on the following Mg^{2+} insertion.

An EL CELL® ECD-3-Nano electrochemical dilatometer (ED) (< 5 nm resolution) was employed to track the volume changes during cyclic voltammetry (5 mV s^{-1}) of MXene electrodes in aqueous 1 M $MgSO_4$ and 0.5 M K_2SO_4. The heart of the ECD-3-nano is a three-electrode cell with the upper working electrode sealed by a thin gold foil. There is a stiff glass frit with a fixed position in between working and counter electrodes. An activated carbon film (YP50F, Kuraray, Japan) was used as a counter electrode as well as the quasi-reference electrode (OCP = -0.1 V *vs.* Ag/AgCl). This device measures the height changes without any interference from the counter electrode. For better comparison of experiments done with different reference electrodes, all potentials are displayed vs. Ag/AgCl.

Results and discussion

To explore the K^+ pre-intercalation effects on capacitive performance in Mg^{2+} containing electrolyte, Figures 1a and 1b show the CVs obtained in the lab-made three-electrode cell using $Ti_3C_2T_x$ as the working electrode. Without K^+ pre-intercalation, Mg^{2+} intercalation/extraction into $Ti_3C_2T_x$ is in a steady state after 25 cycles (Figure 1a). After K^+ pre-intercalation, more Mg^{2+} intercalates the electrodes, as evidenced by comparing the current densities *j* in Figure 1a and 1b. This behavior is more clearly seen in Figure 1c, which shows the volumetric charge density variations with cycles obtained in a dilatometer three-electrode cell, in which the upper line (full symbols) represents charging and the lower line (hollow symbols) corresponds to discharging. Without K^+ pre-intercalation, Mg^{2+} intercalation/extraction is reversible after tens of cycles as evident from nearly overlapping charge density profiles, i.e., 100% columbic efficiency. On the other hand, K^+ ion intercalation and extraction is very asymmetric (different charge densities during charge and discharge) and it can be assumed that K^+ ions still remain between MXene layers to a certain extent. After the K^+ pre-intercalation for 50 cycles, the cell was washed carefully with Millipore water and then switched to Mg^{2+} with the same electrode. Consequently, many more Mg^{2+} ions were intercalated into MXene, as a larger charge density was measured compared to the case without K^+ pre-intercalation (compare black and blue symbols in Fig. 1c). However, the characteristic behavior observed during K^+ ion intercalation remains, as shown by asymmetric charge densities, i.e., 74 % columbic efficiency.

To investigate the Mg^{2+} insertion after pre-intercalation with K^+ in more detail, CV curves were measured as a function of scan rate (Figure 2a and b). Larger intercalation capacitance values after K^+ treatment further confirm that more Mg^{2+} cations were insertion into $Ti_3C_2T_x$. Figure 2c shows that K^+ pre-intercalation increases the capacity for Mg^{2+} insertion, consistent with findings reported in Figure 1. At the same time, the scan rate dependence of the capacitance remains about the same after the K^+ ion treatment, suggesting that the kinetic of Mg^{2+} extraction form the interlayer spaces is not improved.

The actuation properties were tested using electrochemical dilatometry. Figures 3a and b show the CVs and corresponding electrode displacements. To enhance the effect of pre-intercalation, we performed the pre-cycling in K_2SO_4 for 200 cycles, instead of 50 cycles, followed by Mg^{2+} intercalation after the electrolyte exchange. The results were compared with experiments performed in only K_2SO_4 or $MgSO_4$. As the sample area remains constant during the test, the height change is directly proportional to the change in the electrode volume. The electrochemical dilatometry shows that the Mg^{2+} ions intercalation initially results in the volume contraction up to ~23% and little volume changes were observed in the case of K^+, in agreement with the previously published data.[5] In general, the contraction behavior is assigned to negative surface charges which are partially compensated by the cations reducing electrostatic repulsion between MXene layers. But it has also been reported that the ion size plays a role as well in the mechanical sample response.[17, 29] After pre-cycling in aqueous K_2SO_4, the volume is less contracted when Mg^{2+} ions intercalate, ca. 16~17%. This demonstrates the pretreatment by K^+ ions mitigate the deformation of $Ti_3C_2T_x$ electrodes. This might be related to the remaining K^+ trapped in between the MXene layers and consequently pre-straining the MXene electrodes , resulting in less contraction with more Mg^{2+} insertion. Alternatively, the pre-intercalated K^+

changes the surface charges modifying the interaction of the Mg^{2+} with the MXene layers. There is also less hysteresis observed on charge-discharge (Fig. 3b).

Although electrochemical dilatometry offers a convenient way to detect ion intercalation induced strain during cyclic voltammetry, it does not provide access to mechanical properties of the material or information about spatial variations of the volume change. CR-AFM has emerged as a powerful tool for quantitative characterization of the elasticity of materials on nanometer length scales. Here, the AFM tip in contact with the electrode behaves as a simple harmonic oscillator with a characteristic contact resonance frequency. This frequency can be measured by exciting the AFM tip and can be translated into the Young's modulus, *E,* of the material using a tip calibration procedure and mathematical models describing the AFM cantilever dynamics[24]. Therefore, *in situ* CR-AFM was employed herein to track the Young's modulus variations of MXene electrodes in aqueous $MgSO_4$ at first. Upon Mg^{2+} intercalation, the contact resonance frequency shifts to larger values, indicating a stiffer $Ti_3C_2T_x$ structure. The corresponding increase in E is associated with a stiffening of the $Ti_3C_2T_x$ electrode in the normal-to-the-plane direction, and is consistent with contracting inter-layer distance[17] and overall electrode contraction (Figure 3b). Figure 4a shows the nanoscale maps of Young's modulus E upon Mg^{2+} intercalation. Heterogeneities within each map can be interpreted as local variations in Mg^{2+} ion concentration. To analyze the local changes in E, the histograms of the E maps where fitted using two Gaussian functions to represent the local variations (Figure 4b and 4c). When the positions of the Gaussian functions are plotted versus the applied potential, two different behaviors can be observed. The regions represented by the lower Young's modulus E_1 shifts almost linearly whereas the positions represented by the higher Young's modulus E_2 shows a hysteretic behavior (Figure 4c). These two different behaviors could be interpreted as two different Mg^{2+} insertion sites, similar to shallow and deep adsorptions sites as discussed for Mg^{2+} ions from EQCM measurements.[13] It can also be seen that even at the highest potentials, the distribution of Young's modulus is very heterogeneous suggesting that some areas of the sample do not take on Mg^{2+}. On average, Young's modulus changes from about 3 to 9 GPa (a 300% change) upon ion intercalation. After extraction of Mg^{2+} ions back to OCP *i.e.*, -0.2 V, the *E* distribution was close to that of the original state. This points out that the tip shape remained unchanged throughout the CR-AFM scans and the changes in Young's modulus are unambiguously originated from Mg^{2+} ions intercalation/extraction. Some irregularities in the images in Figure 4a stem from instrument drift, which means the areas shown in Figure 4a are not exactly the same.

When K^+ cations were intercalated, the MXene showed less contraction compared to only Mg^{2+}, without K^+ pre-intercalations. The CR-AFM images recorded in aqueous $MgSO_4$ after K^+ pre-intercalation are shown in Figure 5a. Compared to Figure 4a, the distribution of Young's modulus is more homogeneous at higher potentials. This suggests that more MXene volume takes part in the uptake of ions. As in the previous case, the measured distribution of Young's modulus can be fitted using two Gaussian distribution functions, and one linear and one hysteretic response is observed (Figure 5b). However, the addition of K^+ into the interlayer space of $Ti_3C_2T_x$ results in less changes in Young's modulus, which spans values between 5 and 7.5 GPa (a 50% change, Figure 5c).

It has been shown that K^+ intercalation improves the charge storage of Mg^{2+} ions. The exact origin of this phenomenon is unclear at this point. Here we want to discuss two possible factors which could play a key role. First, the intercalation of K^+ can change the interlayer spacing between the MXene layers making it easier for the bigger Mg^{2+} ions to intercalate. However, electrochemical dilatometry shows very little volume changes and the electrode only slightly contracts after K^+ intercalation (Figure 3b). In addition, the trend of the scan rate dependence turns out to be comparable, which is not expected with an increased layer spacing (Figure 2c). In addition, our previous work showed constant layer spacing upon K^+ intercalation as demonstrated by *in situ* XRD.[17] Second, the intercalation of K^+ ions changes the surface chemistry of the MXene sheets, which affects the intercalation of Mg^{2+} and might affect the degree of solvation with which the Mg^{2+} intercalates.[30] This can strongly affect the interaction strength between the intercalated ions and MXene. This is supported by the reduced electrode contraction when K^+ ions are pre-intercalated (Figure 3b), which is a measure for the interaction between the ions and MXene layers.

Conclusions

We have demonstrated novel insight into the K^+ pre-intercalation effects on the changes of electrochemical charge storage and its kinetics, as well as mechanical and actuation properties for Mg^{2+} intercalation into MXene electrodes. The increase in capacitance can be explained by an increased amount of intercalated Mg^{2+} ions when MXene is pre-intercalated with K^+ ions. However, the intercalation kinetics is unchanged. Spatial mapping of Young's modulus changes using CR-AFM reveals that more electrode volume participates in the Mg^{2+} ion uptake when K^+ is pre-intercalated. This will most likely result in a more homogenous mechanical stresses distribution improving long term applications. In addition, it was found that the pre-intercalation of K^+ reduced the actuation properties slightly which could be interesting for applications which are not based on actuation where mechanical deformation needs to be eliminated since stress generated by the ion intercalation affects the electrode porous structure, dimensions and mechanical integrity, which may lead to poor electrical contacts and increased internal resistance. We believe this work will be an important initial step for quantitatively unraveling the charge storage processes in intercalation compounds from the MXene family of materials in the context of choice of proper electrolytes combinations to tune the charge storage and mechanical as well as actuation properties of the electrodes. We believe that it will motivate more systematic studies toward achieving stable electrodes with high capacities for both supercapacitors and multivalent-ion batteries or explore MXenes for actuator applications.

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