Solving the Capacitive Paradox of 2D MXene using Electrochemical Quartz-Crystal Admittance and In Situ Electronic Conductance Measurements

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Fast ion adsorption processes in supercapacitors enable quick storage/delivery of significant amounts of energy, while ion intercalation in battery materials leads to even larger amounts of energy stored, but at substantially lower rates due to diffusional limitations. Intercalation of ions into the recently discovered 2D Ti$_3$C$_2$T$_x$ (MXene) occurs with a very high rate and leads to high capacitance, posing a paradox. Herein, by characterizing the mechanical deformations of MXene electrode materials at various states-of-charge with a variety of cations (Li, Na, K, Cs, Mg, Ca, Ba, and three tetraalkylammonium cations) during cycling by electrochemical quartz-crystal admittance (EQCA, quartz-crystal microbalance with dissipation monitoring) combined with in situ electrochemical quartz-crystal impedance, light is shone on this paradox. Based on this work, it appears that the capacitive paradox stems from cationic insertion, accompanied by significant deformation of the MXene particles, that occurs so rapidly so as to resemble 2D ion adsorption at solid-liquid interfaces. The latter is greatly facilitated by the presence of water molecules between the MXene sheets.

1. Introduction

MXenes, a recently discovered large family of early transition metal carbides and carbonitrides, represent a class of 2D materials that have shown much promise in electrochemical energy storage applications, such as battery and supercapacitor electrodes. These 2D materials are so labeled because, they are produced by the selective etching of the A-group layers (mostly groups 13 and 14) from the MAX phases and to emphasize their similarities to graphene. The MAX phases, in turn, are a large (>70 members) family of layered hexagonal transition metal carbides and nitrides. The most studied MXene to date has been Ti$_3$C$_2$T$_x$ produced by HF etching of Ti$_3$AlC$_2$ powders. When aqueous HF etching is carried out, the MXene surfaces are typically terminated by O, OH and/or F. Because the stoichiometry of these terminations varies, the formula M$_{n+1}$X$_n$T$_x$, where T$_x$ stands for a general surface termination, is used. More recent results have shown that Ti$_3$C$_2$T$_x$ electrodes have large volumetric capacitances and perform at high rates. Spontaneous intercalation of a variety of single- and multiply-charged cations, together with highly reversible electrochemical insertion of the same cations has been well documented for Ti$_3$C$_2$T$_x$ in aqueous electrolytes.

In sharp contradistinction to the slow intercalation of ions usually observed in layered materials for battery applications (intercalation of ions into these materials proceeds slowly and quite often in the form of first-order phase transitions), perfect capacitive behavior was observed for Ti$_3$C$_2$T$_x$ even at quite high charge and discharge rates.

A similar phenomenon was observed for the 2D MXene and for 2D MnO$_2$ (birnessite) and ortho-Nb$_2$O$_5$ polymorph electrodes, presenting an electrochemical capacitive paradox of the entire family of energy storage materials, (or “intercalation pseudocapacitance”). The paradox stems from the fact that these electrodes not only can store relatively large amounts of charge per unit volume or mass, but discharge at rates that are quite rapid indeed. This work is a first attempt to understand how these materials apparently combine some of the best attributes of batteries and capacitors. A variety of ab initio based methods of structural characterization of ortho-Nb$_2$O$_5$ polymorph electrodes were currently carried out for elucidating the intrinsic high charging rates of this material at the atomic scale.
interconnected open channels of the electrode structure result in facile diffusion between the intercalation sites, which in turn resulted in high specific energy.

Herein we propose a new approach based on a combined methodology of electrochemical quartz-crystal admittance, EQCA, in situ electronic conductance and electrochemical impedance to resolve the capacitive paradox of 2D Ti$_3$C$_2$T$_x$ composite electrode coatings. This was done by quantifying the potential-dependent, non-uniform composite electrode deformations in a variety of aqueous electrolytes. As a result, a self-consistent, mesoscopic view of the ions’ insertion/extraction processes into Ti$_3$C$_2$T$_x$ electrodes has emerged. This study was supplemented by electrochemical impedance probing the extent of the capacitive electrode behavior in the extended range of applied frequencies. The existence of shallow and deep-adsorption sites in the electrode coatings together with inserted water molecules is suggested to explain the capacitive paradox of 2D Ti$_3$C$_2$T$_x$ at different charging rates.

2. Results and Discussion

2.1. Morphology and Electroanalytical Features of 2D Ti$_3$C$_2$T$_x$ Electrodes

The morphologies of the electrode slurry components and of the composite electrodes, covering the surface of a gold-coated quartz-crystal (QC), are shown in Figure 1a–d, respectively. As seen in Figure 1a, the average size of the gold particles and free space (or pores) between them are much smaller than the characteristic hydrodynamic parameter, $\delta$, the velocity decay length, which defines the distance at the electrode/solution interface across which the shear wave oscillation loses its intensity by a factor of $e$ (i.e., 2.718). For a 5 MHz QC in contact with dilute aqueous solutions $\delta$ is close to 0.24 µm, and thus the crystal surface is considered flat at the scale of $\delta$. The layered Ti$_3$C$_2$T$_x$ micrometer-sized particles with a rough external surface (Figure 1b) are electrically and mechanically connected by carbon black particles and PVdF fibrils (Figure 1b,c, respectively) (see also schematics of the composite electrode in Figure 1e).

The Ti$_3$C$_2$T$_x$ agglomerates are rigidly attached to the crystal surface by PVdF fibrils (as evidenced by the lack of coated-crystal dissipation when measured in air) forming a continuous, porous electrode coating. The insertion/extraction of ions to/from the Ti$_3$C$_2$T$_x$ particles results in periodic changes of their shape and volume in response to changes in electrode potentials (Figure 1e). As a consequence, due to clamping of the electrode particles, the mechanical deformation of the entire composite electrode layer becomes essentially non-uniform. The description of the complicated solid-liquid interactions originating from variations in the effective electrode layer thickness, $h$, and its permeability length, $\xi$, upon ion insertion/extraction is part of the hydrodynamic admittance problem and is dealt with herein.

Figure 2 summarizes the basic electroanalytical features of thin composite Ti$_3$C$_2$T$_x$ electrode coatings (active mass $\approx$ 60 µg cm$^{-2}$) on a QC surface. Cyclic voltammetric curves (CVs) in Figure 2a–c are plotted as differential specific gravimetric capacitances (Fg$^{-1}$) vs. $E$ (relative to a Ag/AgCl electrode). The nearly rectangular CV loops, as well as only a minor effect of scan rates (Figure 2a) and solution concentration (Figure 2b), on the specific gravimetric capacitance (53–56 Fg$^{-1}$) are more reminiscent of supercapacitive nanoporous carbon electrodes than intercalation-type Li-ion battery electrodes. Figure 2c compares CVs of...
the Ti$_3$C$_2$Tx electrode under study with that of a similar mass micro-mesoporous BP2000 composite carbon electrode. Although the specific gravimetric capacitance of the latter is slightly larger (~66 F g$^{-1}$) and the capacitive character of its CV response is somewhat more pronounced, the striking similarity between both responses is evident. Figure 2d clearly shows that EQCA can be effectively used for tracking capacitance changes during long-term cycling of Ti$_3$C$_2$Tx electrodes with different cut-off potentials.

2.2. Why Gravimetric Sensing is not Sufficient and Full EQCA Analysis is Required

As noted above, the capacitive character of the Ti$_3$C$_2$Tx electrodes during cycling is in dramatic contrast with common thermodynamic and kinetic limitations observed during charging of more typical Li-ion battery intercalation materials,[9] presenting an electrochemical paradox. This paradox is solved herein by analysis of the two components of the hydrodynamic admittance of the Ti$_3$C$_2$Tx electrodes related to the:

i) the change in mass during charging and discharging and
ii) electrode deformation in response to variations in the inserted ion’s charge and size for a variety of alkaline, alkaline-earth and tetraalkylammonium (TAA) cations.

In case of nanometer-sized porous or non-porous carbon particles and related composite electrodes, dissipation of oscillation energy is practically absent, and the frequency shift, $\Delta f$, can be directly related to the mass changes of inserted ions, viz. $\Delta m = -\Delta f/C_m$, where $C_m$ is a sensitivity factor equal to 0.056 Hz/ng cm$^{-2}$ for a 5 MHz crystal. Then $\Delta m$ can be converted
to ionic population changes, $\Gamma$ (nmol cm$^{-2}$), assuming the mass changes are due to those of the unsolvated cations, $M_i$, and cationic charge, $z_i$; assuming:

$$\Gamma = z_i \Delta m/M_i$$  

(1)

A comparison of the raw EQCA data for the alkaline metal chloride series presented in Figure 3b with their related CVs shown in Figure 3a show clear periodic changes of the resonance width $\Delta W$ (green curve, left y-axes in Figure 3b) with sweeping potential (red dashed lines, right y-axis in Figure 3b). These changes are significantly smaller than those of $\Delta f$ (black dotted lines, left y-axis in Figure 3b) especially for the bulkier cations. If one neglects the dissipation-induced changes of $\Delta W$, $\Gamma$ can be calculated from Equation 1. For the case of Li$^+$ insertion (top panel in Figure 3c) the slope of the experimental $\Gamma$ vs. $Q$ plot (dotted black points in Figure 3c) is a factor of 1.54 larger than that of the Faradaic line (red dashed line in Figure 3c). This result implies that 0.65 moles of H$_2$O are inserted with each inserted Li-ion.

In contrast, insertion of K$^+$ or Cs$^+$-cations (panels labeled KCl and CsCl in Figure 3b) are characterized by smaller slopes of the experimental $\Gamma$ vs. $Q$-plots than those for the Faradaic one, implying a mass loss. One interpretation of this result is that at least some of the water molecules between the layers are replaced by the inserted cations. In the Na$^+$ case, the agreement between Faraday’s theory and our experimental results is excellent (see panel labeled NaCl in Figure 3b).

However since $\Delta W$ cannot be ignored, a new alternative approach is proposed here, which takes into account changes in both $\Delta f$ and $\Delta W$ caused by the accompanying electrode deformations for all metal cations studied.

As an example, Supporting Information Figure S1 details this approach for Cs$^+$. The related raw EQCA data are shown in Supporting Information Figure S1a, whereas the experimental frequency shift, $\Delta f_{\text{exp}}$ and that calculated from the passed charge, $\Delta f_{\text{mass}}$, are compared as functions of $E$ in Supporting Information Figure S1b. The maximal difference between these two frequencies ($\approx 10\%$) is reached at $-0.6$ V. Then $\Delta f_{\text{mass}}$ is subtracted from the $\Delta f_{\text{exp}}$, resulting in the corrected frequency change, together with the (minor) potential dependence of the resonance width shift. The results are presented in Supporting Information Figure S1c. The potential-induced shift of the corrected frequency and the resonance width changes can now be assigned to the deformation of the Ti$_3$C$_2$Tx electrode particles during Cs$^+$ insertion. In other words, $\Delta f$ and $\Delta W$ become input parameters for the hydrodynamic admittance model of the electrode layer composed of intercalated particles, carbon black and PVdF binder.

2.3. Hydrodynamic Spectroscopy of Ti$_3$C$_2$Tx Composite Electrode Coatings and Principles of QC Admittance Analysis

The use of EQCA as an important analytical technique has advanced considerably during the last two decades and has been successfully used for studying a variety of the processes occurring with coated QCs in different media.$^{[16,17]}$ The outstanding contributions of several research groups should be specially acknowledged and is documented in some review articles.$^{[18,19]}$ However, viscoelastic models,$^{[20]}$ valid for various polymeric coatings, are not suitable to describe charging processes in composite intercalation electrodes. Here we rely instead on our previous work devoted to hydrodynamic spectroscopy of chemically and structurally non-homogeneous composite electrode coatings (see ref. $^{[12]}$ and references therein), that was subsequently used to quantitatively interpret large potential-induced deformations of charged LiFePO$_4$ particles.$^{[21]}$ A summary of the approach used is provided below; further details can be found in Section 1 of the Supporting Information.

Figure 3. a) CVs of Ti$_3$C$_2$Tx in 0.025 M solutions of alkaline metal cation chlorides and b) accompanying time dependencies of $\Delta f$, $\Delta W$ and electrode potential (depicted by black, green and red lines, respectively. c) Adsorption of cations, $\Gamma$, as a function of electrode charge density, $Q$. Dashed lines are calculated using Faraday’s law.
The hydrodynamic spectroscopy model requires measuring the crystal admittance of porous electrode layers in contact with liquids of different viscosities and densities that, in turn, are characterized by a variety of velocity decay lengths, δ. This model links the experimentally measured admittance components, normalized by liquid density, ρ, i.e., Δf/ρ and ΔW/ρ, to δ through a number of porous electrode structure parameters.[12] The governing equations for the total frequency and width changes of the resonance peaks are given in the Supporting Information (Equations S1 and S2, respectively). Two major geometric parameters of the electrodes’ coatings, namely, their effective thickness, h, and permeability length, ξ, are obtained by fitting the admittance model results to the experimentally measured values, of Δf/ρ and ΔW/ρ.

The permeability length, ξ, which affects the resisting force from non-homogeneous solids acting on the liquid, is a characteristic lateral length of the electrode layer reflecting its porosity. The results of hydrodynamic spectroscopic analysis of the Ti₃C₂Tx electrode coatings under study are shown in Supporting Information Figure S2. Using Supporting Information Equations S1 and S2 the initial (i.e., prior to application of a potential scan) values of h₀ and x₀ were found to be 0.42 µm and 0.24 µm, respectively. The same equations were applied to the potential-dependent changes of Δf and ΔW in order to determine the periodic changes of Δh and Δξ from their initial values, h₀ and x₀.

It is pertinent to note the mesoscopic scale of the structural information obtained by EQCA since as was mentioned above for dilute aqueous solutions, δ ≈ 0.24 µm, is the characteristic length of the problem. EQCA can thus easily discriminate between the rigid attachment of the solution components in the pores of the electrode coatings narrower than δ, and a situation in which significant dissipation of the oscillation energy takes place in pores wider than δ. Unlike in situ X-ray diffraction (XRD), EQCA traces changes in potential-dependent, non-uniform deformations of the entire composite electrode layer, including those of polymeric binders, which depend on their mechanical properties. The advantage of EQCA over in situ dilatometry,[22] on the other hand, is its ability to sense even small changes in the electrode layer permeability during ion insertion/extraction linked to the changes of the electrode’s porosity.

2.4. Hydrodynamic Admittance Approach to Insertion of Alkaline, Alkaline-Earth and TAA Cations

Similar to the Cs⁺ case, the same hydrodynamic admittance approach was applied to the entire series of alkaline, alkaline-earth and TAA cations. The goal was to probe the van der Waals gaps between the layers of the Ti₃C₂Tx multilayers by inserting cations of different charges and sizes. The differential specific gravimetric capacitance of the Ti₃C₂Tx electrode for the alkaline, alkaline-earth metal and TAA cations, are shown in Figure 4a,c,e, respectively. The variation of the geometric parameters of the electrode layer, h and ξ are shown in Figure 4b,d,f, respectively. As the potential shifts more negative than 0.2 V, the cation concentration between the layers increases and the responses of h (left y-axis in panels b, d, and e) and ξ (right y-axis in b, d, and e) to that increase is quite telling and can be summarized as follows: 1) When the cations radii are large, such as those for TMA⁺, TEA⁺ and TBA⁺, after a region in which h and ξ do not change much with potential, their size dominates the response, and both h and ξ increase (Figure 4f). 2) In the case of Na⁺-cations, (red points in Figure 4b), the changes are quite small. This indirectly implies that the expansion due to the intercalation of these cations is balanced by an enhanced attraction between the Ti₃C₂Tx sheets with increasing Na⁺-cations concentration between the sheets. Note that even in this case, at the most negative potentials, contraction dominates over expansion. 3) For alkali metal ions larger than Na⁺, (purple and blue points in Figure 3b), size matters more than charge and the lattice expands at negative potentials. 4) For the alkaline-earth cations (Figure 4d), charge is more important than size and the interlayer distance shrinks at negative potentials. 5) The response of Li⁺-cation (black points in Figure 4b) is instructive since it behaves more like the alkaline-earth cations although it is a singly charged cation and its size is quite small.

Said otherwise the most important consideration on how the MXene layers respond, is the ratio of the ionic charge to its radius. Higher ratios lead to shrinkage; lower ratios lead to expansion. We thus conclude that the proposed hydrodynamic model quantifies the deformation of the composite electrode layer in the presence of different cations and consistently explains the dependence of the composite electrode deformation on the ion’s charge and size.

The above quantitative analysis of potential-dependent deformations arising in the Ti₃C₂Tx electrode upon cationic insertion was performed when the electrode reached a stationary state. However, a large benefit of EQCA is its ability to reflect, with high sensitivity, also the initial changes in the electrode structure when it is first immersed into electrolyte solutions or even pure solvents. For example, Supporting Information Figure S3 displays transient long-time changes in Δf (black line) and ΔW (blue line) upon repetitive charge-discharge cycling of Ti₃C₂Tx electrode (red lines). Figure 2d shows the subsequent cycling behavior of the same electrode. During the initial 45 cycles, the electrode charge increased by a factor of 3 (not shown), whereas the changes in the average values of Δf and ΔW approach approximately −190 and +160 Hz, respectively (Supporting Information Figure S3). This result is in excellent agreement with the changes in interlayer distances in Ti₃C₂Tx measured by in situ XRD after immersion of the electrode into Li-ion containing aqueous solution as compared to its subsequent potential-dependent changes.[4] This implies that the initial expansion of the Ti₃C₂Tx particles is due to the insertion of cations (replacing H⁺ in T = OH) and water molecules between the Ti₃C₂Tx layers, until a steady-state condition is reached.

Some may argue that the results obtained on very thin coatings onto the QC (50–80 µg cm⁻²) do not necessarily translate to characteristics of practical electrodes, typically containing 2–10 mg cm⁻² of active electrode mass. In contrast to the former coatings (i.e., related to the QC) the latter composite electrodes are calendared and tested in coin or Swagelok cells under moderate pressure. The question arises as to whether the reversible capacitance and the mechanical changes of these two types of electrodes, with entirely different cell geometries and extents of electrode compression, are also comparable. In order to answer this
important question we performed in situ electronic conductance measurements using interdigitated Pt microelectrodes\(^{23}\) covered with Ti$_3$C$_2$T$_x$, and electrochemical impedance measurements with rolled Ti$_3$C$_2$T$_x$ electrodes were tested in Swagelok cells. These two techniques probe electrode deformations indirectly, however, this (even qualitative) information, sheds more light on the dependence of electrode deformations of composite electrodes of different thicknesses and under different clamping conditions.

2.5. In Situ Electronic Conductance Measurements

This technique tracks electron transport both across individual intercalated particles and the contact areas of neighboring particles in the composite Ti$_3$C$_2$T$_x$ electrode as a function of the inserted cation. A similar experimental setup was used previously for characterizing ionic adsorption into nanoporous carbon electrodes.\(^{13–15}\) Supporting Information Figure S4a presents a schematic of such conductance measurements, with Pt microarray electrodes completely covered by a composite electrode coating. Supporting Information Figure S4b shows a plot of the electronic conductance of a Ti$_3$C$_2$T$_x$ electrode as a function of $E$ during insertion of Li$^+$. Since for a nearly perfect capacitive response the electrode charge during linear potential scan is proportional to the applied potential, the straight-line relationship between the conductance and potential implies proportionality between the conductance and mobile charge carrier concentrations, and thus concentration-independent mobility of the related charge carriers. Note, that the composite electrode contained Ti$_3$C$_2$T$_x$ (94 wt%) and PVdF (6 wt%); no carbon black was added in this case. Thus, Ti$_3$C$_2$T$_x$ appears to behave like a heavily doped semiconductor or a semi-metal.

In contrast to the conductance of a continuous coating, the conductance of porous composite electrode coatings inevitably depends on the content of the conducting carbon black and/or extent of composite electrode compression. Moreover, for a moderately thick electrode film of $\approx$5 μm on to microarray electrodes, the conductance exhibited a gradual decrease during cycling. This happens, for example, when transitioning from single-charged Li$^+$ to double-charged alkaline-earth cations, which can cause a contraction of the electrode particles (Supporting Information Figure S5a,b). Note that the 5-μm film used here is about an order of magnitude thicker than the hydrodynamic thickness of the electrode layer on the QC surface, and an order of magnitude thinner than that used in the clamped Swagelok cells.

We also explored the effects of Li$^+$-to-Mg$^{2+}$ ion exchange on the CV and the related electronic conductance responses of the electrodes. This was carried out by adding Mg$^{2+}$ ions to

![Figure 4. Capacitances of Ti$_3$C$_2$T$_x$ electrode obtained from the CVs measured at a scan rate of 50 mV s$^{-1}$ in 0.05 M chloride solutions of a) alkaline, c) alkaline-earth and e) TAA cations series. The corresponding potential changes in the effective electrode layer thicknesses, $h$ (open symbols, left hand $y$-axis), and their permeability lengths, $\xi$ (closed symbols, right hand $y$-axis) for b) alkaline, d) alkaline-earth, and f) TAA cations series. Fitting was done with the use of Supporting Information Equations S1 and S2.](image-url)
a neat LiCl solution (Supporting Information Figure S5c,d). Since the Mg$^{2+}$ ions, as shown by the EQCA study, resulted in significantly larger contractions of the Ti$_3$C$_2$Tx particles compared to those for Li$^+$-ions (Figure 4) it is reasonable to assume that when the electrode coating is relatively thick and is tested under non-clamped conditions, its electronic conductance can significantly deteriorate because of the relatively large dimensional changes of individual neighboring electrode particles. The PVdF fibrils mechanically connecting the intercalation particles to the entire composite electrode coating may be not elastic enough to ensure its complete relaxation. To confirm this hypothesis we carefully examined the properties of rolled and clamped Ti$_3$C$_2$Tx electrodes using more elastic PTFE binder.

### 2.6. Rolled and Clamped PTFE-Based Composite Ti$_3$C$_2$Tx Electrodes

We first checked that the galvanostatic and CV modes of charging, performed at comparable rates, led to similar differential specific gravimetric capacitances (Supporting Information Figure S6). Figure 5a shows, as an example, CV curves obtained for scan rates varying from 0.5 to 100 mV s$^{-1}$. Qualitatively, the CVs measured with the rolled electrodes are similar to those measured with electrode coatings attached to the QC surfaces (Figure 2a). Note that the active mass of the former is about 2 orders of magnitude larger than that deposited on the QC surface. Although the absolute capacitances for both electrodes are quite similar, because of their larger thicknesses and despite the clamping that decreases interparticle contact resistance, the rolled electrodes show a somewhat larger dispersion of the capacitances as a function of scan rates.

Figure 5b presents a more quantitative view of the effects of the kinetic limitations of the electrode capacitances. Least squares fitting of the double log plot of the capacitance measured at $-0.2$ V reveals a perfect linear dependence (with correlation coefficient close to 1) with a slope equal to 0.95. This slope is significantly higher than the value of 0.5, characteristic of diffusion limited processes. Notably, however, it is much closer to the unit slope characteristic of completely reversible behavior with the expected independence of capacitance on scan rate. Note however, that due to the log-log nature of the plot, even a 5% decrease of the slope (i.e. from 1 to 0.95) results in a notable decrease in the electrode capacitance at high scan rates (inset in Figure 5b).

Figure 5c demonstrates two important experimental observations. First, at the slow scan rate of 2 mV s$^{-1}$ (black and orange curves for LiCl and MgCl$_2$ solutions, respectively, in Figure 5c), the gravimetric capacitances are a weak function of electrode mass loading (compare cells 1 and 2 for LiCl and MgCl$_2$). Second, even more important, is that after replacing the LiCl solution by its MgCl$_2$ counterpart, for the same electrode, a much higher capacitance was recorded for the latter (compare dashed orange curve with solid black line in Figure 5c), consistent with the results obtained by EQCA.

Figure 6 compares the capacitances of thin QC electrode coatings to those of thick electrode coatings studied in Swagelok cells. The agreement is quite good for all the cations tested (values of crystallographic radii for different cations were taken from the same literature source\cite{24}). Note that the measured...
capacitances for the double-charged cations are two times lower than those of their single-charged counterparts (given by the top horizontal dotted line in Figure 6). Since theoretically the factor should have been two, the fact that it is not strongly implies that insertion of double-charged cations is limited by the number of sites available in the host electrode during its charging. However, this thermodynamic factor per force overlaps with a kinetic one, revealing that insertion of double-charged cations is slower than that of single-charged cations. This conclusion is supported by all three techniques used in this work.

It is reasonable to assume that small-mass (single to a few particles layer thick) electrode coatings on QC surfaces would be less affected by interparticle contact resistances compared to those of moderately thick coatings under non-clamped conditions in a typical in situ conductance experiment. However, flexible well-formed rolled electrodes, tested in Swagelok cells under pressure, reveal again a diminished effect of the potential-dependent changes of the particles sizes and their contact resistances on the electrode capacitance as follows from the CV study in LiCl and MgCl₂ solutions at two different scan rates (Figure 7a) and by using electrochemical impedance (Figure 7b–d). At a slower scan rate (2 mV s⁻¹), the CVs in the MgCl₂ solutions differ from those in the LiCl solutions by a much higher increase of current towards both ends of the scanning potentials which is reminiscent of a large electrode deformation in the presence of Mg²⁺ and the related slower insertion kinetics discussed below.

For consistency’s sake, the capacitive character of the CV of the Ti₃C₂Tₓ electrode was compared with that of the electrochemical impedance measured in the same solutions. The low-frequency domain of the Nyquist plot is expected to be linked to the gravimetric differential capacitance, C (the imaginary part of impedance Z''=−1/ωC, where ω is the angular frequency of the AC current) and should thus be comparable to that obtained from related CV curves. In contrast, the high-frequency domain of impedance spectra reflects the rate of interfacial charge-transfer processes, that are not immediately seen from the CVs measured at much slower rates intrinsic to that technique. Figure 7c shows that the low-frequency domains of
the electrode spectra measured in LiCl and MgCl₂ solutions are quite comparable, and can be presented by a constant-phase element (CPE) with a fractional exponent $\alpha = 0.94$. The high-frequency domain of the electrode impedance in MgCl₂ reveals a depressed semicircle whereas such a semicircle is absent in the spectrum measured in LiCl (inset in Figure 7c). This semicircle can originate from ion transfer across the entire interface of Ti₃C₂Tx particles in contact with the electrolyte solution.

Because the BET surface area of the Ti₃C₂Tx powder is around 23 m²g⁻¹, the capacitance taken at the semicircle’s maximum translates to about 1 μF cm⁻². This value is by an order of magnitude lower than that typically expected for a variety of electrodes in aqueous solutions. This can be explained by incomplete accessibility of the internal surface area of particles in thick rolled electrodes in the high-frequency range. In this way, we assigned the high-frequency semicircle of the Nyquist plots to Mg²⁺ transfer, which appears thus much slower than the transfer of singly charged Li⁺-ions. Figure 7b presents the plot of the effective low-frequency capacitance vs. log frequency calculated from the experimental Nyquist plot in the MgCl₂ solution (circles) and from the best fit (black solid line) we extract a CPE coefficient of 58 F s⁻α⁻¹ g⁻¹, and a CPE exponent $\alpha = 0.94$. This linear plot compares well with the linear capacitance vs. log scan rates plot for the CV (inset in Figure 5b) revealing consistency between the data obtained by both techniques.

Finally, in view of the non-capacitive features of the CV plots of Ti₃C₂Tx electrodes in MgCl₂ solutions towards the edge of electrochemical stability window, the electrode was cycled 100 times at a scan rate 1 mV s⁻¹. When the impedance measured immediately after the 100 cycles (red solid diamonds in Figure 7d) was compared with that before cycling (black solid diamonds in Figure 7d), it was obvious that the long-term cycling of the electrode in the MgCl₂ solution results in further retardation of the interfacial ion transfer in the high-frequency domain (inset in Figure 7d) of the spectra, and in a diminished value of the CPE exponent in the low-frequency domain typical of aging of the active electrode mass. This explanation is also consistent with our in situ electronic conductance measurements (Supporting Information Figure S5).

The electrochemical impedance characterization of the Ti₃C₂Tx/PTFE electrode in contact with LiCl and MgCl₂ solutions presents further evidence for the highly reversible character of cation insertion into this rolled electrode. The capacitive line of the Nyquist plot (Figure 7c) is the low-frequency limit of the finite-space Warburg behavior which describes equally the processes of ion adsorption and intercalation on the electrode surface and its interior, respectively. These two processes are typically distinguished by much slower interfacial and diffusion kinetics for intercalation processes. This certainly is not the case for Ti₃C₂Tx showing a clearly expressed capacitive-type impedance in a quite wide frequency range. This capacitive character of the impedance was also recently reported for ortho-Nb₂O₅ and N- and B-doped graphene sheets electrodes. However, the exponent of the CPE of the low-frequency impedance for both these electrodes is smaller than that for Ti₃C₂Tx suggesting more perfect capacitive behavior of the latter.

Despite the capacitive impedance, the relatively large changes of the potential-dependent interlayer spaces in this electrode obtained by in situ XRD, the characteristic dependencies of the electrode layer deformations on the cation’s charge and size tracked by EQCA (Figure 4) imply a typical intercalation-type process, leading to a capacitive paradox for these multilayered Ti₃C₂Tx electrode.

2.7. The Origin of the Capacitive Paradox

Deeper insight into the origin of this capacitive paradox can be gained by answering the following question: Should the intercalation-type process be as clearly expressed for cations insertion into delaminated (dispersed) Ti₃C₂Tx electrode coatings as is the case of its multilayered analog, or, on the contrary, its behavior is entirely capacitive? To answer this question we ran a series of preliminary experiments on delaminated Ti₃C₂Tx electrodes. The CVs, raw EQCA data and in situ electronic conductance of the delaminated Ti₃C₂Tx electrode coating characterized in 0.05 M LiCl solution are shown in Supporting Information Figure S7a–c, respectively.

The delaminated electrode consists of randomly stacked single, or few-sheets of Ti₃C₂Tx (3 MXene layers on average), i.e. differs from the multilayered Ti₃C₂Tx by the absence of long-range order along [0001]. Remarkably, in this case, $\Delta f$ and $\Delta W$ remain constant during the Li-ion insertion/extraction process (Supporting Information Figure S7b), which in turn implies that the electrode layer does not deform. It follows that the related frequency changes can be interpreted in this particular case as originating from gravimetric changes only.

The perfect linear dependence of the electronic conductance of the delaminated Ti₃C₂Tx coatings with potential (Supporting Information Figure S7c) is quite similar to that found for the multilayered coatings (Supporting Information Figure S5b,d) revealing their similar electronic properties, in particular, a potential-independent charge-carrier mobility. Interestingly, single-atomic-sheet crystals of 2D NbSe₂, and MoS₂ show similar features for the mobilities of the electronic charge carriers. Hence there is no reason to believe that the electronic properties of the completely delaminated Ti₃C₂Tx coatings are significantly different from their multilayered counterparts. This implies quite similar conditions for catiologic adsorption in both cases. The initial swelling of the multilayered Ti₃C₂Tx coatings occurring spontaneously when in contact with the solution at open-circuit potential smears out the distinct differences that are known for the conventional ion intercalation and ion adsorption processes. The capacitive paradox of the multilayered Ti₃C₂Tx MXene electrodes is thus resolved by invoking the idea that adsorbed cations are electrochemically inserted between partially swollen Ti₃C₂Tx layers. This conjecture is consistent with a response for which kinetic limitations and first-order phase transitions are absent that are quite similar to those observed during reversible 2D ion adsorption.

Exfoliated and multilayered Ti₃C₂Tx MXenes thus appear to differ only in the value of their specific gravimetric capacitances, rather than in the shape of their CV curves since the gap between the layers in the multilayered sample is opened to a larger extent from the solution side rather than in the
particle’s interior. This can be formally accounted for by invoking the existence of shallow-adsorption sites near the edges of the multilayer particles that are water-rich, and deep-adsorption sites with higher activation energies for ion adsorption in the particle’s interior (see Figure 8a). After a large number of cycles, and/or by slowly charging and discharging, one can assign the increase of the cathodic current close to −0.6 V at slow scan rates to ion accommodation on the deep-adsorption sites (Figure 8b).

In contrast to the facile ions desorption from the shallow-adsorption sites, desorption of ions from the deep-adsorption sites only occurs with a significant overvoltage, close to 0 V vs. Ag/AgCl (see Figure 5a.c and 7a). This conjecture fully explains the good Faradaic efficiency of the charge-discharge processes at low charging rates and the gradual increase of the capacitance upon long-term cycling or time. The reactions on the newly exposed internal surfaces can also explain, to some extent, the increase in the electrode impedance (Figure 7c,d). At medium and fast scan rates, the adsorption is thus most likely limited to shallow-adsorption sites.

The gravimetric specific capacitances obtained for singly charged cations by EQCA is, on average, ≈54 F g⁻¹ (Figure 6), or 12.5 mAh g⁻¹ (assuming the voltage to amplitude approximately be 1 V) which translates into a Li⁺ adsorption level of x = 0.09 or Ti₃C₂O₂Li₀.09. When deriving this stoichiometry, we took into account the latest DFT and XPS studies showing that the electrode surfaces exposed to the solution are terminated by hydroxyl ions, up to a stoichiometry of Ti₃C₂(OH)₂.[31]

In the case of the divalent cations, the ideal composition for Mg²⁺-ions insertion should be Ti₃C₂O₂Mg₀.09 whereas an insertion level, Ti₃C₂O₂Mg₀.07, was reached experimentally. The obtained capacitances are somewhat lower, presumably because insertion of divalent cations is more kinetically limited compared to their singly charged counterparts. The full capacitance of the exfoliated Ti₃C₂Tₓ flakes estimated by DFT for the insertion of Li⁺-cation is much higher and can reach a stoichiometry Ti₃C₂O₂Li₂.[32] This gives a rough estimate of the extent of the Ti₃C₂Tₓ interlayer opening, and hence the fraction of the shallow-trap sites in the studied case is at a level of ca. 4.6%, thus providing hope for the expected significant increases in both specific power and energy of optimally delaminated materials of the MXene family.

3. Conclusions

The complementary use of EQCA, in situ electronic conductance and electrochemical impedance measurements of multilayered 2D Ti₃C₂Tx MXene electrodes allowed us to simultaneously track their state of charge and ion-induced deformations, along with studying the insertion kinetics of a large variety of cations. The following conclusions can be made: 1) Highly charged small cations contract the interlayer spaces of 2D Ti₃C₂Tx electrodes, whereas larger cations with smaller charges expand the interlayer spaces. 2) The electrochemical capacitive paradox of 2D Ti₃C₂Tx MXene electrodes can be explained by conjecturing the presence of two types of cationic adsorption sites in the interlayer gaps of the Ti₃C₂Tx layers: shallow and deep. The general conclusion is that the partially exfoliated 2D electrodes, with interlayer gaps filled with ions and water molecules are characterized by a perfect capacitive response over a surprisingly wide range of charging rates. 3) The specific capacitance estimated for Li-ion insertion from slow-scan rate CV curves or low-frequency impedance, ≈53 F g⁻¹, translates to the specific capacity of 14.7 Ah kg⁻¹, and hence a specific energy of 14.7 Wh kg⁻¹. The estimated maximal specific power from the available CV studies is 5.3 kW kg⁻¹. Hence the charge and discharge, with a characteristic time constant of 10 s obtained from the specific energy to the specific power ratio, results in a Ti₃C₂(OH)₂ electrode that simultaneously possesses high specific power and high (for supercapacitors) specific energy. 4) Very high charge-discharge rate of the Ti₃C₂(OH)₂ electrode is advantageous compared to conventional intercalation compounds, being second only to their 2D single-sheet analogs. These conclusions suggest that exfoliation and/or breaking up the individual Ti₃C₂Tx flakes would lead to even higher capacitances at higher cycling rates.
4. Experimental Section

Synthesis of multilayered Ti$_3$C$_2$T$_x$ MXene powders and corresponding electroanalytical experiments carried out on composite MXene/PTFE/carbon black laminate electrodes have been described previously.[4] The methodology of EQCA experiments with thin composite electrode coatings on microarray interdigitated Pt electrodes and in situ electronic conductance measurement protocol were described in detail elsewhere.[13,14] The same salts and types of electrochemical cells were used as previously reported for nanoporous carbons.[15] The fabrication of spray-coated multilayered 2D Ti$_3$C$_2$T$_x$ electrodes on the QC was similar to that described for the nanoporous carbon coatings[13–15,15] except that herein the electrode slurry composition was: 80 wt% MXene powder, 10 wt% SuperP carbon black and 10 wt% polyvinylidene difluoride (PVdf) binder.

Supporting Information

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

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