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**Investigations on
 V_2C MXenes and $\text{Mo}_{4/3}\text{B}_2$ MBenes
as Anode Materials for Lithium-Ion Batteries**

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Investigations on V_2C MXenes and $Mo_{4/3}B_2$ MBenes as Anode Materials for Lithium-Ion Batteries

The recently developed two-dimensional class of layered materials, MXenes and MBenes, has attracted attention as potential electrode materials in Li-ion batteries due to their high theoretical capacity, long cycling stability and fast conductivity. This work investigates transition metal carbides and borides with respect to their application potential as future anode materials for LIBs using XRD, SEM, EDS, XPS, CV, GCPL and EIS. Firstly, the impact of $\sim 1\%$ Mn-doping in V_2C , i.e. $Mn-V_2C$, was investigated. XRD patterns reveal a $> 10\%$ enlarged interlayer spacing and EIS show a $> 25\%$ reduced charge transport resistance in $Mn-V_2C$, leading to an increase in specific capacity. GCPL studies show $> 30\%$ larger reversible capacities in $Mn-V_2C$ compared to V_2C . Secondly, the impact on battery performance of the usage of different etching solvents during the synthesis of $Mn-V_2C$ was investigated. XRD, SEM and EDS measurements reveal a higher amount of residual MAX phase and a more dense and closed accordion-like morphology in $Mn-V_2C(NaF)$ (synthesized with $HCl + NaF$), compared to $Mn-V_2C(LiF)$ (synthesized with $HCl + LiF$). GCPL studies show significantly larger specific capacities in $Mn-V_2C(LiF)$ by almost 50% compared to $Mn-V_2C(NaF)$. Thirdly, first principle measurements on novel $Mo_{4/3}B_2$ MBenes were conducted. From XRD, SEM and CV the existence of pure MBene phase could not be unambiguously confirmed, the synthesis therefore needs further improvements. All materials under study showed the importance of a well-performed and clean synthesis process of MXenes and MBenes when used as anode materials for LIBs.

Untersuchung von V_2C MXenen und $Mo_{4/3}B_2$ MBenen als Anodenmaterialien für Lithium-Ionen Batterien

Die vor Kurzem entwickelte zweidimensionale Klasse von Schichtmaterialien, MXene und MBene, hat aufgrund ihrer hohen theoretischen Kapazität, Zyklenstabilität und Leitfähigkeit Aufmerksamkeit als potenziell neues Elektrodenmaterial für Li-Ionen-Batterien (LIB) erhalten. In der vorliegenden Arbeit werden Übergangsmetallcarbide und -boride im Hinblick auf ihre potentielle Anwendung als zukünftige Anodenmaterialien für LIBs mit Hilfe von XRD, SEM, EDS, XPS, CV, GCPL und EIS untersucht. Zunächst wurde der Einfluss von $\sim 1\%$ Mn-Dotierung in V_2C , also $Mn-V_2C$, diskutiert. XRD zeigt einen $> 10\%$ erhöhten Schichtabstand und EIS zeigt einen $> 25\%$ verringerten Ladungstransportwiderstand in $Mn-V_2C$, was zu einer Erhöhung der spezifischen Kapazität führt. GCPL zeigt eine um $> 30\%$ erhöhte Kapazität in $Mn-V_2C$ im Vergleich zu V_2C . Im Anschluss wurde der Einfluss auf die Batterieperformance bei der Verwendung verschiedener Ätzmittel während der Synthese von $Mn-V_2C$ MXenen untersucht. XRD, SEM und EDS zeigen eine höhere Menge an restlichem Vorläufermaterial und eine dichtere und geschlossene Morphologie mit einer hohen Menge an $Na_5Al_3F_{14}$ auf der Partikeloberfläche in $Mn-V_2C(NaF)$ (synthetisiert mit $HCl + NaF$), verglichen zu $Mn-V_2C(LiF)$ (synthetisiert mit $HCl + LiF$). GCPL zeigt daher eine um fast 50 % erhöhte Kapazität in $Mn-V_2C(LiF)$ im Vergleich zu $Mn-V_2C(NaF)$. Zuletzt wurden Messungen an neuartigem $Mo_{4/3}B_2$ MBene durchgeführt. XRD, SEM und CV konnten die Existenz reiner MBene-Phase nicht eindeutig bestätigen, die Verbesserung der Synthese ist daher unumgänglich. Alle untersuchten Materialien zeigten die Wichtigkeit eines gut durchgeführten und sauberen Syntheseprozesses von MXenen und MBenen.

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1 Introduction

The rapid advancement of technology in recent decades has dramatically increased the demand for efficient and reliable energy storage solutions. Among these, Li-ion batteries (LIB) have become the cornerstone of portable electronic devices, electric vehicles, and renewable energy systems. Their popularity originates from their high energy density, long lifetime range, and relatively low self-discharge rate [1]. However, the dependence on these batteries grows, and so does the need to improve their performance, safety, and sustainability [2, 3].

Current LIBs primarily rely on materials such as graphite for the anode and various Li compounds for the cathode [3]. While these materials serve well, they still have limitations in terms of energy capacity, charging speed, and environmental impact [4]. The search for better materials is essential to meet the increasing energy demands and to address issues related to battery life, safety and sustainability. While ongoing research focuses a lot on novel materials on the cathode side [5], investigations on the anode side are also important, because it is an similar crucial bottleneck in LIB development. Thus, this thesis focuses on exploring novel anode materials that could one day revolutionize LIB technology.

One promising class of materials are MXenes and MBenes, firstly developed in 2011 [6]. These are a family of two-dimensional materials composed of transition metal carbides, nitrides, or borides which have unique properties that make them highly attractive for the potential use as anode material in LIBs [7]. MXenes offer high electrical conductivity and their large surface area as well as tunable properties allow a high Li storage capacity, thereby potentially overcoming the limitations of graphite [8].

One of those candidates investigated in this work is the MXene V_2C , which is already well explored and known to the scientific community [9–11]. Aiming to further increase the battery performance of this material by altering physical and electrochemical properties, this work investigates on the impact of a Mn-doping in V_2C . But not only the final battery performance of future LIB materials is of importance. A successful despite facile synthesis of MXene materials is also significant as it potentially enhances the sustainability of energy storage and reduces costs. Therefore, the impact on the battery performance of the usage of different etching solvents applied during the synthesis process of MXenes will be discussed. In particular, Mn-doped V_2C MXenes produced by using $HCl + LiF$ or $HCl + NaF$ will be characterized. Ultimately, this work performs first principle investigations on the whole new $Mo_{4/3}B_2$ MBene used as an anode material for LIB. This thesis uses a set of well-established advanced techniques. They range from physical methods like XRD, SEM, EDS and XPS for structural characterizations of the materials, to electrochemical methods like CV, GCPL and EIS in order to evaluate the overall battery performance.

The outline of this thesis is as follows: Chapter 2 introduces the theoretical background, the experimental setup and the material class of MXenes and MBenes. Chapter 3 presents the results of Mn-doping in V_2C MXenes. Chapter 4 discusses the influence of different etching solvents used during the etching process of MXenes. Chapter 5 provides first investigations on $Mo_{4/3}B_2$ MBene. Finally, a summary in chapter 6 concludes this work.

2 Theoretical Background and Experimental Methods

2.1 Physical Characterization Methods

Powder X-Ray Diffraction

Powder X-ray diffraction (XRD) is a common method to determine the crystallographic structure of a material. Monochromatic light is focused on a powder sample in an angle θ with a wavelength λ in the length of two crystal layers d . The incident rays then interfere constructively with the sample, when Bragg's law is obeyed:

$$n\lambda = 2d\sin(\theta) \quad (2.1)$$

Here, $n \in \mathbb{N}$ denotes an integer number. The obtained Bragg pattern is then detected, processed and analyzed with respect to their crystalline phases and composition. The powdered material exhibits random orientation, thus it is necessary to scan through a range of 2θ angles to capture all potential diffraction directions of the lattice. The Bragg reflections occurring in the recorded diffractograms are compared with reference entries in the crystallographic databases of ICSD [12]. A more detailed description of XRD is provided in [13].

The measurements shown in this work were carried out by Ilse Glass on the Bruker D8 ADVANCE ECO diffractometer with copper $K\alpha$ radiation ($\lambda(K\alpha_1) = 0.15406 \text{ nm}$ and $\lambda(K\alpha_2) = 0.15444 \text{ nm}$) at the Institute of Geosciences at Heidelberg University. The sample preparation is carried out in two steps. In order to obtain a uniform distribution of the powder, it is first manually dispersed with isopropanol in a mortar by hand to a satisfactory finesse. The resulting dispersion is then evenly applied to a silicon sample carrier. The measurement is performed continuously and the integrated intensity is stepwise (typically $\Delta 2\theta = 0.02^\circ$) recorded.

Scanning Electron Microscopy & Energy-dispersive X-Ray Spectroscopy

Scanning electron microscopy (SEM) is a technique to obtain information about surface topology and morphology of a sample. It is an imaging tool which uses an electron beam to resolve the sample surface [14]. The intensity of the scattered electrons are detected, whereby two processes are of crucial importance: First, the secondary electrons, that are inelastically scattered electrons with a low kinetic energy of a few electronvolts. They feature only a low penetration depth of a few nanometers, thus imaging the surface of the sample with a resolution down to 10 nm. Second, the back-scattered electrons, that are elastically scattered electrons with a higher kinetic energy which originate from deeper

layers in the material. A more detailed introduction to SEM is given in [14, 15].

Energy dispersive x-ray spectroscopy (EDS) gives precise information about the atomic composition in a sample by taking advantage the same interactions. The interaction between the electron beam and the sample thereby also lead to X-ray emission. The incident electron beam may excite a bound electron in an inner shell forcing a high-energy electron from an outer shell to fill the created electron hole, while emitting a photon. These X-rays contain distinctive information about characteristic transitions. In EDS, these emitted X-rays are detected and analyzed in a histogram to achieve an accurate elemental distribution function.

Topographical measurements shown in this work were performed on a Zeiss SEM (type LEO 1530) and a JEOL SEM (type JSM-7610F) of the Institute for Physical Chemistry of the Heidelberg University. The sample is prepared by initially attaching self-adhesive Carbon tape to the device-specific sample holder. Next, a small quantity of the powder sample, approximately the amount that fits on the tip of a pair of tweezers, is spread onto it. A layer of approx. 10 nm Au was subsequently applied onto the sample by using a blazers sputtering device (type Union SCD 004), which reduces electrical charge of the sample and thus minimizes imaging errors.

Elemental Analysis

In some cases, when characteristic transitions observed via EDS are in a similar energy range, the differentiation between elements can be very challenging or even impossible. In these cases, another characterization method needs to be taken into account. The elemental analysis (EA) measures the amount of Carbon (C), Hydrogen (H) and Nitrogen (N) in a sample [16]. Thus, this method is often referred as CHN analysis. In this method, the sample is explosively burned in an oxygen-rich atmosphere thereby generating gases (CO_2 , H_2O , NO_x). This gas mixture is passed over a heated, high-purity tungsten contact in order to remove the excess oxygen and to convert the nitrogen oxides (NO_x) into molecular nitrogen (N_2). Subsequently, the gas mixture is separated using gas chromatography and the individual components are supplied to and analyzed by a thermal conductivity detector. Finally, the amount of C, H and N in the sample can be quantified.

EA shown in this work were performed at the Organic Chemistry Institute of the Heidelberg University by C. Vetter using the Elementar Vario MICRO Cube.

X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a method to analyze the elemental composition, the oxidation and the valence state on the surface of a sample. The basic principle of XPS relies on the photoelectric effect [17]. Monochromatic X-rays are focused on a sample and electrons energetically closely bound to the nucleus are emitted. The binding energy E_B , which has to be overcome to emit an electron, is given as follows:

$$E_B = h\nu - (E_{kin} + \Phi) \quad (2.2)$$

Here, $h\nu$ is the energy of the X-ray photons with the frequency ν and the Planck constant h , E_{kin} is the kinetic energy of the emitted electrons detected in the measurement and the

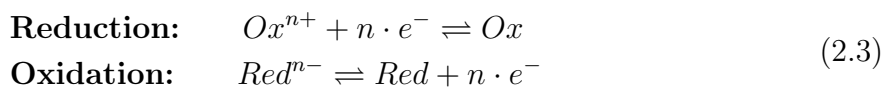
work function Φ is a correction factor for the instrument, which correlates to the minimum energy needed to release an electron from an atom. A spectrum with characteristic kinetic electron energies is then detected, whereby every element and composition has a unique energy level spectrum and can thus be unambiguously identified. A handbook of X-ray photoelectron spectra is given in [18].

XPS data and corresponding plots and fittings shown in this work were carried out in the working group of Prof. Dr. Michael Zharnikov at the Institute of Applied Physical Chemistry at Heidelberg University using a MAX200 spectrometer (Leybold-Heraeus). It comprises a Mg $K\alpha$ X-ray source (200 W) and an hemispherical analysator. For sample preparation, a copper sample holder was initially roughened with sandpaper. A piece of pure In metal was then applied to the holder and pressed down with a spatula. The oxidized surface of the In was then removed using a scalpel. Next, a thin layer of the powder sample was evenly spread over the shiny In surface and pressed lightly with a spatula to form a uniform film. To enhance adhesion between the In and the powder, the powder film was covered with Al foil and pressed hand-tight in a vice using a press matrix. Finally, any loose, excess powder was removed with a fine brush. The resulting sample holder has a firm, uniform powder sample film on an In surface.

2.2 Electrochemistry

Galvanic Cell

The basic principle of electrochemical energy relies on the conversion of chemical energy into electrical energy and vice versa. This can be realized using a so called galvanic cell, which consists out of two electrodes, that are separated by separators with an electrolyte featuring a high ionic but low electric conductivity. In order to close the ionic current in the electrolyte and to perform electrical work, an external circuit can be used to connect the two electrodes. The working principle is based on redox reactions, in which the less noble electrode gets oxidized by loosing at least one electron and the other electrode captures the electron. The reaction formula is given by:



Here, n is the number of electrons involved in each reaction. The electrode in which oxidation and reduction takes place is called anode and cathode, respectively. If the cell is not reversibly (dis-)chargeable, it is considered as a primary cell. In contrast, reversibly (dis-)chargeable cells are called secondary cells, wherein an electric current may be applied to enforce reciprocal reactions for recharging. If the two electrodes are electrically connected by an outer closed circuit, these redox reactions happen because of their electrochemical potential difference.

The potential of an electrode in thermodynamic equilibrium is given by the Nernst equation:

$$E_{\text{electrode}} = E_0 + \frac{RT}{nF} \cdot \ln \left(\frac{a_{\text{Ox}}}{a_{\text{Red}}} \right) \quad (2.4)$$

Here, E_0 , R , T and F denote the standart potential, the universal gas constant, the absolute temperature, and the Faraday constant, respectively. a_{Ox} and a_{Red} describe the concentration dependent activity of the specimen involved in the redox reaction. The voltage of a total galvanic cell (often also referred to as open circuit voltage, OCV) is thus given by the difference of the potentials of the anode and the cathode.

$$E_{\text{cell}} = E_{\text{anode}} - E_{\text{cathode}} \quad (2.5)$$

Lithium-Ion Battery

The most commonly used secondary galvanic cells are Li-ion batteries (LIB). Modern LIBs use intercalation materials as active electrode materials. In these processes, Li^+ -ions diffuse reversibly into interstitial sites while the crystallographic structure remains intact and the volume expansion upon cycling is minimized. Other ways for Li^+ -ions to accumulate into active materials are conversion and alloying processes or a combination of thereof [19]. Since anode materials investigated in this work exhibit pure intercalation processes, the description of conversion and alloying processes will be spared. An illustration of the working principle of a LIB is shown in Figure 2.1. Discharging the battery by intercalating Li^+ -ions into the cathode is called delithiation, while charging the battery by intercalating Li^+ -ions into the anode is thereby called lithiation.

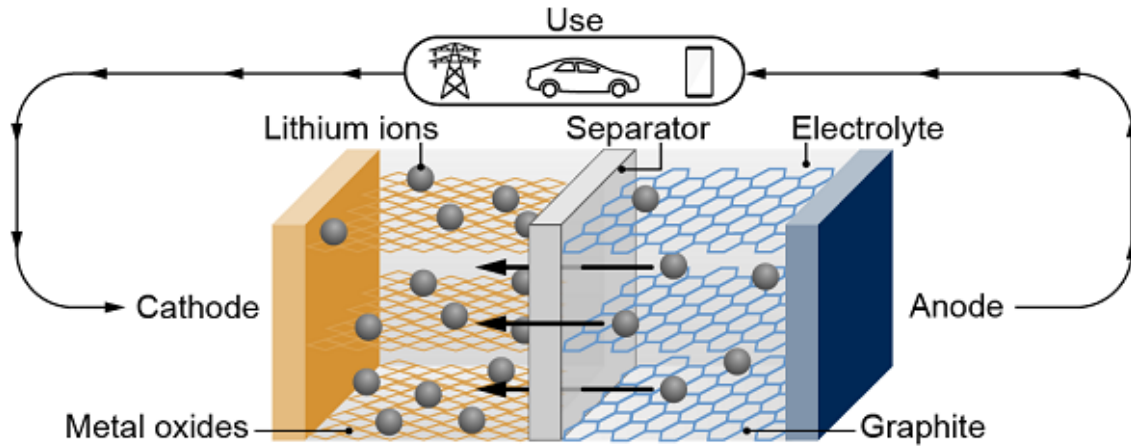


Figure 2.1: Illustration of the working principle of a LIB while discharging. It consists out of the cathode (usually a metal oxide) and anode (usually graphite) isolated by a separator soaked in electrolyte. Due to the high ionic conductivity of the separator, Li^+ -ions can diffuse directly from the anode to the cathode and recombine with the electrons that flow via an outer circuit to the cathode. Extracted from [20].

Most commonly, graphite is used on the anode, and different composite materials are used on the cathode side [3]. Important to mention are LiCoO_2 , $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC) or LiFePO_4 (LFP).

Certain parameters are useful to evaluate the overall battery performance: The specific capacity shows the amount of charge that is stored or released per mass of active material, in mAh g^{-1} . The cycling performance describes how often a battery can be charged and discharged without mayor losses in specific capacity upon cycling. The Coulomb efficiency (CE, see eq. 2.8) displays the ratio between charging and discharging capacity in one cycle, while differences of these values may indicate the existence of irreversible reactions taking place. Finally, the rate performance exhibits the ability of a battery to charge/discharge at altering current densities. The specific power density is a measure for the amount of energy that can be stored in the battery in W kg^{-1} . Is is a product of the nominal cell voltage and the specific capacity, normalized by the weight. This description is based on [21–23], in which an in-depth explanation of electrochemistry can be found.

2.3 Electrochemical Characterization Methods

Cyclic Voltammetry

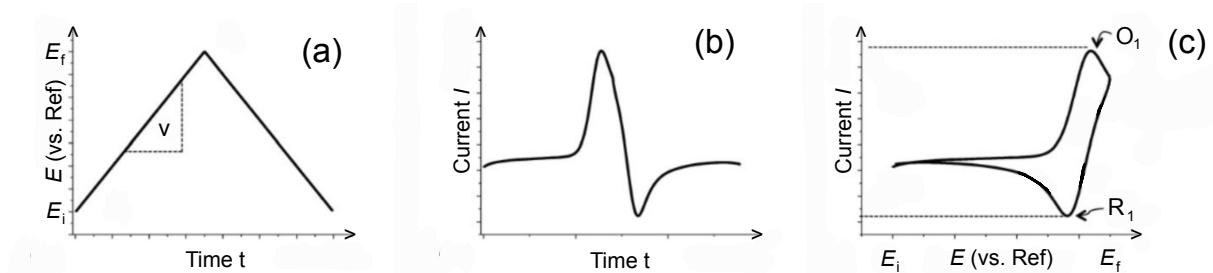


Figure 2.2: Example of a cyclic voltammetry measurement. (a) shows the triangular voltage applied to the cell, (b) the resulting detected current over time, and (c) the final cyclic voltammogram with an exemplary reduction R_1 and oxidation peak O_1 . Extracted and adapted from [24].

Cyclic voltammetry (CV) is a powerful method to investigate electrochemical processes, more specifically, reduction and oxidation processes in a cell. A potential is applied to the working electrode relative to the reference electrode. The process begins with an initial potential E_i , which linearly sweeps to a final potential E_f and then back to E_i in a triangular voltage pattern, see Fig. 2.2a. The sweeping rate used in this work equals $v = dE/dt = 0.1 \text{ mV s}^{-1}$. As to be seen in Fig. 2.2b, the resulting induced current I over time is then detected. The representation of the measured data of cyclic voltammetry measurement, in which the measured current is plotted against the voltage, is called a cyclic voltammogram (see Fig. 2.2c). The presence of peaks (e.g. O_1 , R_1) occurring in CV curves correspond to reduction and oxidation processes, wherein their corresponding potential values give information about the exact processes in literature. A more detailed introduction to CV can be found in [25].

Galvanostatic Cycling with Potential Limitation

Galvanostatic cycling with potential limitation (GCPL) is a technique to investigate the charge and discharge processes, the cyclability and the specific capacity of a cell. Within this method, a constant (dis-) charge current (also called cycling rate) is applied to the battery and its potential profile is measured. GCPL data can provide insights into the type of process occurring. For instance, in a Nernst system, the potential stabilizes near the equilibrium potential of the redox pair, meaning that plateaus in the GCPL potential curves correspond to peaks in a cyclic voltammogram. Also, the amount of charge transferred can indicate the effectiveness of individual processes and the lithium content in the electrode material, reflected in the specific capacity C_{spec} of the cell. The specific capacity of a charging cycle may be obtained by integrating the measured current flow $I(t)$ over time t :

$$C_{spec} = \frac{1}{m} \int_0^t I(t) \quad (2.6)$$

Thereby, m denotes the mass of active material on the electrode. The theoretical, material-specific capacity of an electrode material can be determined using Faraday's law:

$$C_{theo} = \frac{z \cdot F}{m_{mol}} \quad (2.7)$$

Here, z , F and m_{mol} denote the amount of electrons stored in each unit cell, the Faraday constant and the molar mass of the material, respectively. The current and capacity are standardized to the mass load of the active components of the electrode. Anode materials investigated in this work are measured in the voltage range from 0.01 to 3 V. Thus, the contribution of Carbon black (as a constituent of the working electrode, see chapter 2.4) to the specific capacity also needs to be taken into account because of its electrochemical activity in the low voltage range. Furthermore, the Coulomb efficiency (CE), which is a measure of the reversibility of the investigated electrochemical processes, can be extracted from the GCPL data as follows:

$$CE = \frac{\text{discharge capacity}}{\text{charge capacity}} \quad (2.8)$$

Cycling stability is another key factor, indicating the proportion of the original capacity retained after repeated charging and discharging cycles. The combination of specific capacity and cycling stability is generally referred to as electrochemical performance. To ensure reproducibility and prevent deep discharge and/or overcharging effects, a potential limitation between 0.01 and 3 V is applied in the measurements of this work.

Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is a method to characterize the kinetics inside electrochemical systems. Information about e.g. diffusion processes and electric and ionic conductivity may be extracted by triggering their different relaxation timescales. To this end, a small perturbation in the form of a sinusoidal voltage $U(t) = U_m \sin(\omega t)$ is applied to the system, and the responding current $I(t) = I_m \sin(\omega t + \theta)$ is measured. Here, U_m , I_m , ω , t and θ denote the respective amplitudes of the voltage $U(t)$ and the

current $I(t)$, the angular frequency, the time and the resulting phase difference between the applied voltage and the corresponding current, respectively. The impedance Z of the system is then defined as:

$$Z = \frac{U(t)}{I(t)} = |Z|e^{i\theta} \quad (2.9)$$

In this work, EIS measurements were performed using a three-electrode setup (see chapter 2.4 Fig. 2.4). This includes a working electrode, a counter electrode and a reference electrode. The latter one thereby serves to eliminate any effects that are not originating from the working electrode. A small perturbation of 10 mV in a frequency range from 1 mHz to 200 kHz was used. To ensure reproducibility, an OCV of 16h was applied to the cell before the EIS measurement and directly afterwards a second control measurement was performed.

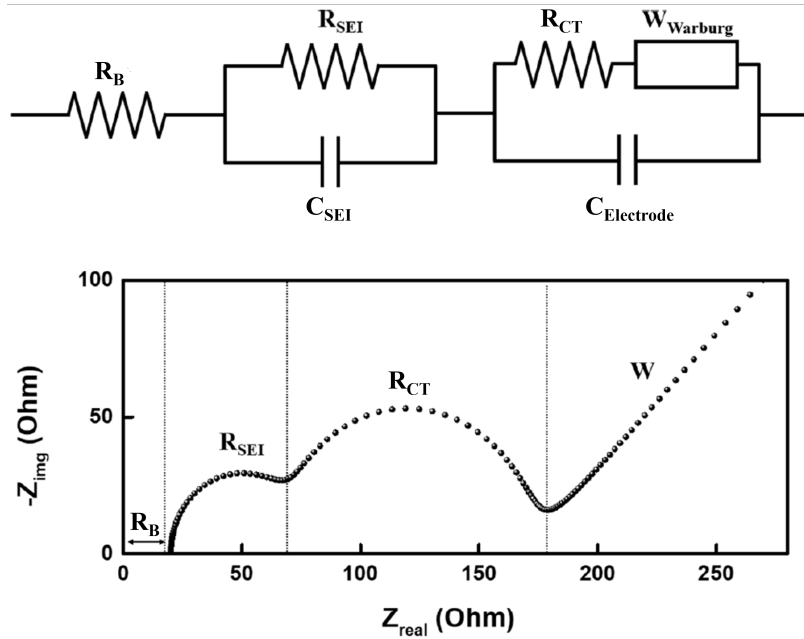


Figure 2.3: Exemplary Nyquist plot of a half cell with a corresponding equivalent circuit above. Plotted is $-\text{Im}(Z)$ over $\text{Re}(Z)$, wherein each data point corresponds to one frequency applied. The plot consists out of three regimes: I. high frequency range corresponding to bulk resistance R_B ; II. mid frequency range corresponding to charge transport properties of the working electrode with typical half circle behavior; and III. low frequency range corresponding to diffusion processes with linear regime. Extracted and adapted from [26].

To analyze the measurements, a so-called Nyquist diagram is usually used, as exemplary shown in Fig. 2.3, which plots the negative imaginary part of the impedance $-\text{Im}(Z)$ against the real part of the impedance $\text{Re}(Z)$, while each data point corresponds to one frequency applied. This allows to distinguish the respective time scales of the characteristic cell components and cell processes, wherein fast processes are represented on the left, slow processes represented on the right side of the diagram. To interpret the impedance

illustrated in these Nyquist plots, a so-called equivalent circuit is generated, which fits the shape of the Nyquist plot and thus delivers information about the system. Typical equivalent elements are a resistance R , a capacitance C , an inductance L , and a Warburg Impedance W . Their impedance's are respectively:

$$Z_R = R, \quad Z_C = \frac{1}{j\omega C}, \quad Z_L = i\omega L, \quad Z_W = \frac{\sigma}{\sqrt{\omega}} - \frac{i\sigma}{\sqrt{\omega}} \quad (2.10)$$

Here, σ denotes the Warburg coefficient and α a parameter introduced to account for the deviation from an ideal capacitor. Figure 2.3 shows exemplary a Nyquist plot and an equivalent circuit of a lithium-ion battery half cell system. It can be split into three regimes. The first regime, an offset of the x-axis, refers to the bulk resistance R_B of the cell (combined resistance of electrolyte, separator and electrodes). The second regime is related to the half-circle shape and relates to the resistance R_{SEI} and capacitance C_{SEI} of the solid electrolyte interfacial layer (SEI), the charge-transfer resistance R_{CT} and the double-layer capacitance $C_{electrode}$. The third regime corresponds to the linearity in the low frequency range and represents diffusion effects of Li-ions on the host material, indicated by the Warburg element $W_{Warburg}$. For the interested reader, a detailed explanation of the elements and the analysis of the electrochemical impedance can be found in [26]. The above description is extracted from [26, 27].

2.4 Electrochemical Setup

This section provides an overview over the electrode preparation and the electrochemical measurement systems used in this work. The electrochemical measurements were performed using a multi-channel VMP3, a VSP potentiostat and a battery cycler (BCS) from BioLogic. The VMP3 potentiostat has two measurement options for electrochemical impedance spectroscopy. The potentiostats have three taps for potential measurement and two current connections. The software used for all devices is "EC-Lab" from BioLogic. To ensure a state of equilibrium, a minimum of 12 h OCV resting time was carried out before each measurement. Both the connections of the VMP3, which are located in a Binder heating cabinet, as well as the connections of the VSP and the BCS are set to constant 25 °C.

Preparation of the Active Material

The active materials investigated in this work were prepared by a hydrothermal assisted in-situ etching method, conducted by Dr. Peng Guo. Firstly, the etching solution was prepared by dissolving 1 g of LiF powder in a 9M HCl solution followed by a magnetically stirring time of 2 h. The etching solution can in-situ form HF solution which exposure is very toxic, the preparation process was thus operated in an HF lab. Afterwards, the precursors (V_2AlC , $Mn-V_2AlC$, $(Mo_{2/3}Y_{1/3})_2AlB_2$) bought from Jilin 11 Technology Co., Ltd) was then immersed into the etching solution. The mixture was transferred to a 50 ml stainless steel autoclave lined with PTFE and heated at 90° for 84 h. The precipitate was collected after centrifugation, washed several times with water and ethanol until the pH value of the solution was above 5, and dried in an oven at 60° for 24 h.

Preparation of the Working Electrode

The electrodes prepared in this work consist out of three main components: active material (AM), Carbon black (CB, Super C65, Timcal) as a conductant and polyvinylidene fluoride binder (PVDF, Solvay Plastics). The exact weight ratio of AM:CB:PVDF was set to be 70:20:10 for the purposes of this work. First, AM, CB and PVDF are weighed. In the next step, this mixture is dissolved in N-methyl-2-pyrrolidone (NMP) using a magnetic stirrer in combination with a stirring fish for 24 h. To increase the viscosity and thus the adhesion, part of the NMP of the mixture is subsequently evaporated in a vacuum drying oven (65°, 12 mbar) for at least 1 h. After creating a suitable viscosity, the paste is applied homogeneously to a mesh-like copper current collector by hand using a spatula. This current collector has a diameter of 10 mm for CV and GCPL measurements, or 18 mm for EIS measurements, a wire diameter of 0.115 mm, and a thickness of 0.25 mm. The coated electrodes are then dried in a vacuum oven for 24 h before being pressed at 10 MPa using a hydraulic press. The electrodes are dried again for several hours before being placed in a glove box with Argon protection atmosphere ($O_2 < 1$ ppm, $H_2O < 1$ ppm) for cell assembly. The reproducibility of the electrochemical measurements depends largely on the quality of the electrode production. The main factors for the quality of the electrodes are: The weighing error, the homogeneity both during mixing and when applying to the copper meshes, as well as the mass loading of the electrodes. As these processes are carried out manually by hand, precise control of these parameters is not fully possible. Depending on the sample and the quantity of weighed material used, the inaccuracy of the measurement data can be estimated to be between 5-10 % on average.

Cell Assembly

In this work, two different cell types were used: The coin cell half cell for CV and GCPL measurements as well as the PAT cell for EIS measurements.

The layout of a coin cell is shown in Fig. 2.4(a). It consists out of 304/316 stainless steel cases, a stainless steel spring, a stainless steel spacer, a Li-foil as a counter electrode (Alfa Aesar, 99,9% metal basis), followed by two layers of separators made of non-woven glass fiber (Whatman GF/D, $d = 12$ mm soaked in 65 μ L electrolyte solution each with usually 1M $LiPF_6$ in 1:1 Ethylenecarbonate (EC) and Dimethylcarbonate (DMC) (Electrolyte LP30, Merck) and the working electrode comprising the active material. After assembly, the cell was sealed using pressure of 30 MPa using a MSK 640-G press by TMAX.

Fig. 2.4(b) shows the layout of the PAT-Cell made by the company EL-CELL. It consists out of a stainless steel main shell with an upper (1) and lower (9) part, a polyethylene insulation seal (2), an upper (3) and lower (8) stainless steel plunger, a Li-foil (4) as a counter electrode, the PAT core (5) with 100 μ L electrolyte and the working electrode comprising the active material (7). The PAT-Core (see Fig. 2.4(c)) made of polyether ether ketone (PEEK) comprises an outer stick ring, a nickel reed contact, a reference ring with Li-coating as a reference electrode, a separator made of non-woven glass fiber (Whatman GF/A, $d = 21.6$ mm) and an inner stick ring.

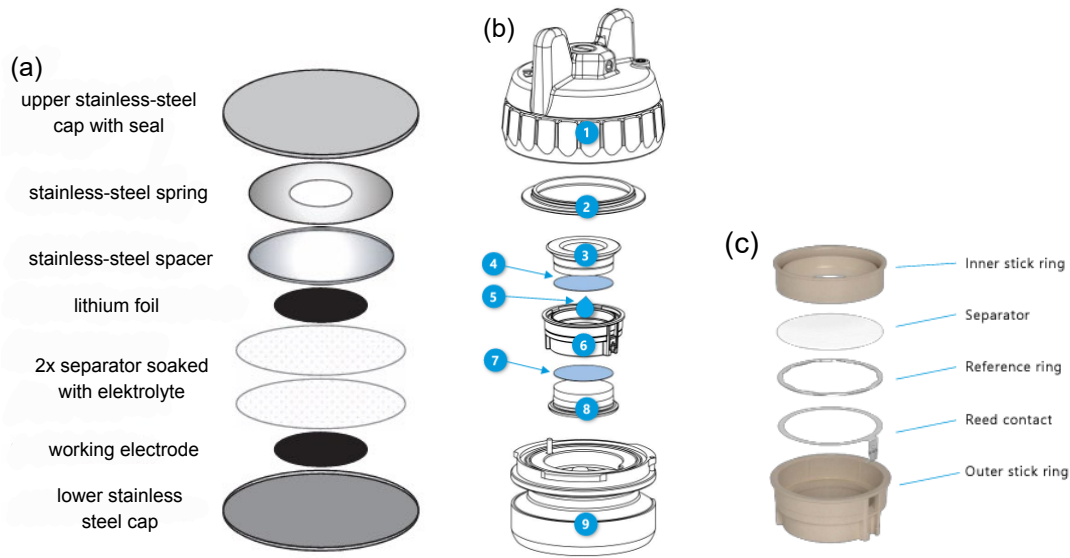


Figure 2.4: (a) Assembly of the coin cell used for CV and GCPL measurements, adapted from [28]. (b) Assembly of the PAT-Cell used for EIS measurements, extracted from [29]. (c) Assembly of the PAT Core for PAT-Cell assembly, extracted from [29].

Blank Measurements of the Coin Cell

In order to determine the contribution of Carbon black (CB) to peaks in cyclic voltammograms and to specific capacity, blank measurements were performed. The electrodes used for these measurements consist out of CB and PVDF in a mass ratio of 90:10.

Fig. 2.5(a) shows a blank CV measurement. Plotted are the first, second and 10th (dis-)charging scans (in black, red and green, respectively) conducted at a scan rate of 0.1 mV s^{-1} . During the first discharge scan (in black), two reduction peaks are observable at $R_{\text{SEI}} = 0.66 \text{ V}$ and $R_{\text{C2}} = 0.01 \text{ V}$. During the first charge scan, two oxidation peaks are observable at $O_{\text{C2}} = 0.14 \text{ V}$ and $O_{\text{C1}} = 0.91 \text{ V}$. In the second and 10th discharge scan (in red and green respectively), only the reduction peak R_{C2} as well as a new peak at $R_{\text{C1}} = 0.83 \text{ V}$ are present. the second and 10th charge scan feature the same peaks which were already observed in the first charge scan. The vanishing of R_{SEI} after the first cycle indicates irreversible behavior and corresponds to SEI formation [30, 31]. The other peaks are identified as redox pairs $R_{\text{C1}}/O_{\text{C1}}$ and $R_{\text{C2}}/O_{\text{C2}}$ correspond to intercalation processes of Li-ions into CB [32]. Fig. 2.5(b) shows a blank GCPL measurement. Plotted is the specific capacity over the first 100 cycles at (dis-)charging currents of 0.1 A g^{-1} . The initial capacity of 378 mA h g^{-1} drops after the first cycle and saturates to 222 mA h g^{-1} . Thus, 20% of weight proportion of CB in the usual working electrodes used in this work contributes with 45 mA h g^{-1} to the specific capacity.

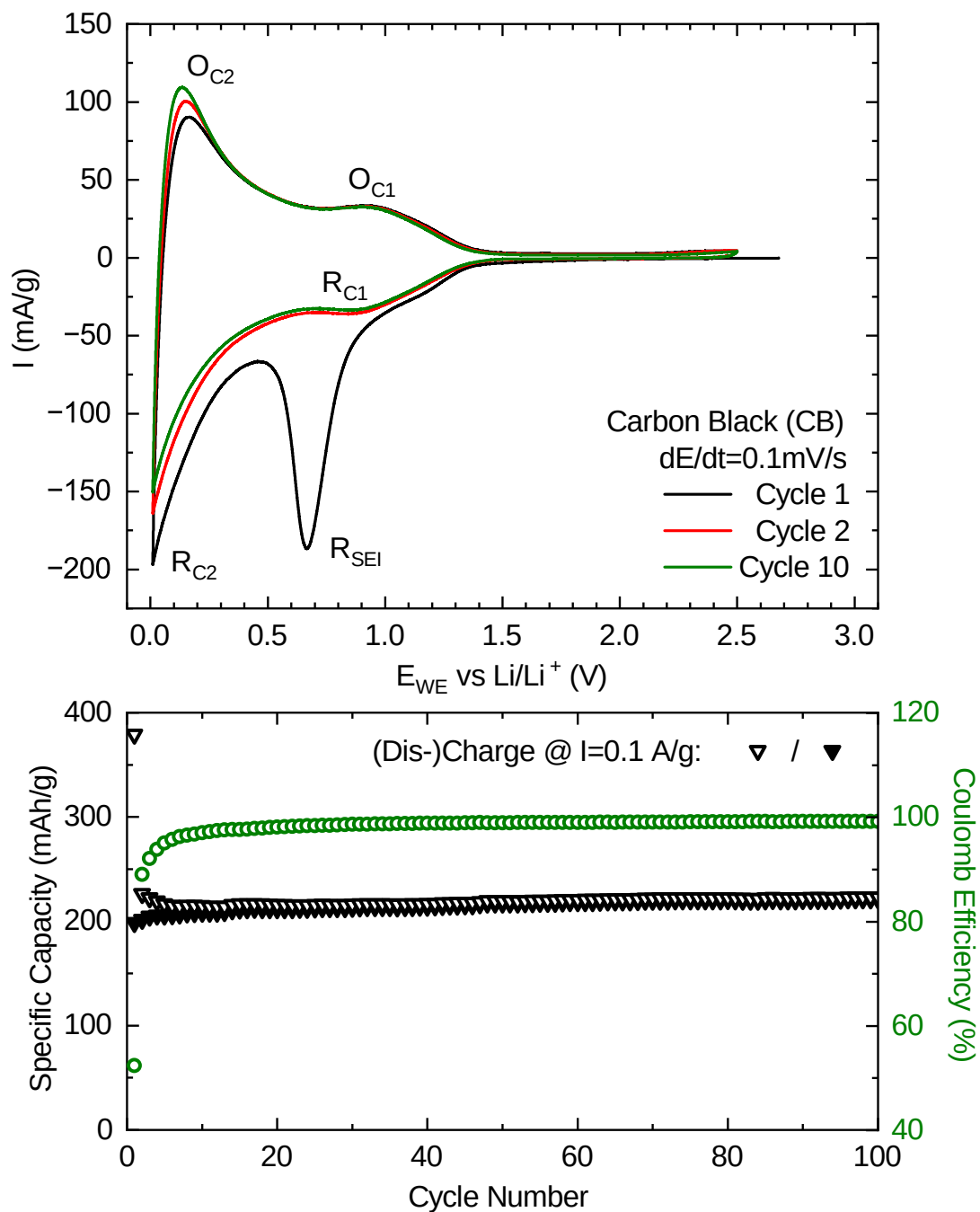


Figure 2.5: CV and GCPL measurements of CB. (a) shows a CV of cycle 1,2 and 10 (in black, red and green, respectively) measured at a scan rate of 0.1 mV s^{-1} . The labels R/O represent distinct reduction and oxidation peaks. (b) shows specific discharge and charge capacities at 0.1 A g^{-1} obtained in the voltage regime from 0.01 to 3 V.

2.5 Introduction to the Material Class of MXenes & MBenes

MXenes are a class of two dimensional (2D) nanomaterials firstly developed in 2011 at Drexel University by Naguib et al. [6]. They promise several advantages like high theoretical capacity, long cycling stability and high conductivity and are thus considered as promising future anode materials for Li-ion battery applications, but also in many other applications like catalysis, electronics and photonics [7, 33]. MXenes are synthesized from a precursor. This parental material has a general structure of $M_{n+1}AX_n$ (short: MAX phase), wherein M represents an early transition metal, A an A-group element and X Carbon or Nitrogen. The synthesis consists out of the selective etching of the A phase from the precursor and the subsequent sonication of the sample, resulting then in the end product "MXenes" [6]. A schematic illustration of the etching procedure is given in Fig. 2.6. The stacking type can thereby be varied by altering $n \in \{1, 2, 3\}$. Etching particular layers is possible due to different interlayer bonding properties. While the bonding between the M and X phases is strong covalent, M-A phases exhibit weaker metallic bonding. The major indication for a successful synthesis of MXene phase is a dominant (002) diffraction peak in XRD pattern. Compared to the precursor material, all other peaks are significantly weakened [34]. Introduced during the synthesis process are so called surface functional groups T_z , wherein i.e. $T \in \{OH, F\}$. These impurity phases may alter the physical and electrochemical properties of the sample and may thus be of crucial importance [35]. When used as an electrode for battery applications, ions can intercalate into the interlayer sites, which became vacant after the successful etching process. The first ever developed MXene was synthesized through exfoliating the Al layer of Ti_3AlC_2 resulting in $Ti_3C_2T_z$ using HF acid [6]. Since HF is highly toxic, more gentle etching procedures with solutions of i.e. $HCl + LiF$ or $HCl + NaF$ are nowadays being used [36, 37].

As disclosed, MXenes are limited to 2D carbides and/or nitrides [6, 38]. But there are also attempts to introduce Boron based 2D materials [39, 40]. Inspired by the structure of MXenes, these so called MBenes can also be synthesized from a precursor material with the structure $M_{n+1}AB_n$ (short MAB phase). Unfortunately, the synthesis of these borides face several complications like phase transformations, only partial etching of Al, and dissolution of the 3D compounds [41]. To strengthen the crystallographic structure, theoretical predictions therefore suggested novel MAB phases with an in-plane vacancy ordering, as specified by $(M'_{2/3}M''_{1/3})_2AB_2$, which were firstly confirmed and successfully synthesized in 2020 via $(Mo_{2/3}Y_{1/3})_2AlB_2$ and $(Mo_{2/3}Sc_{1/3})_2AlB_2$ [42]. By a similar etching procedure as shown in Fig. 2.6, the sample $Mo_{4/3}B_2$ can be synthesized.

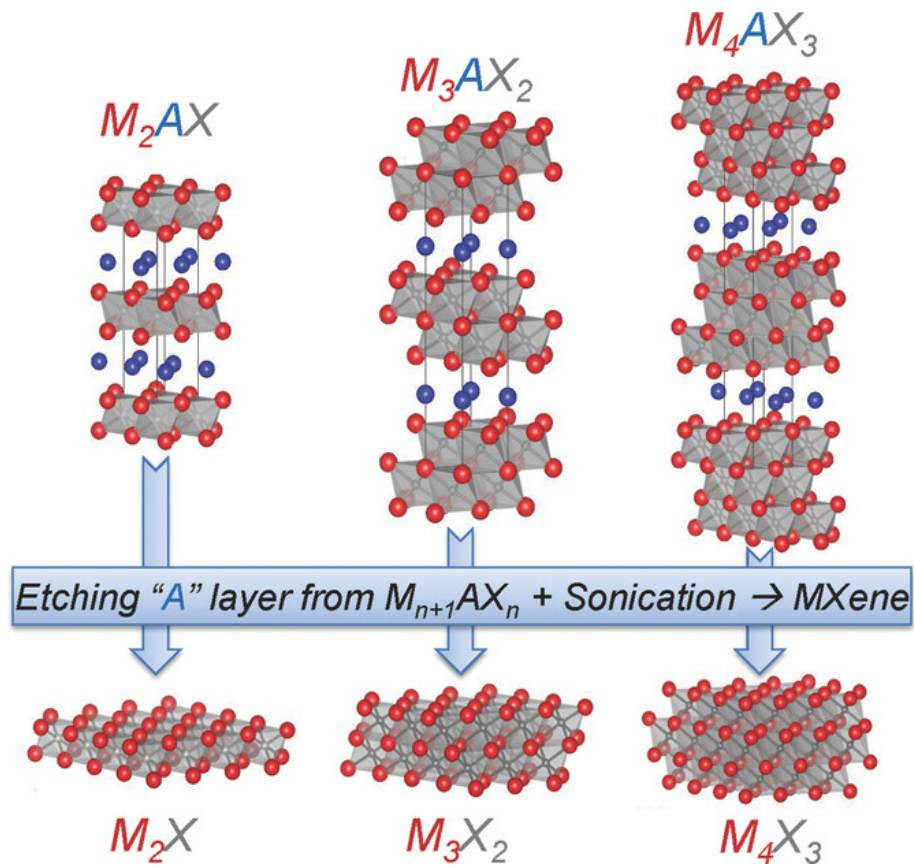


Figure 2.6: Illustration of the etching procedure by exfoliating the A phase of the MAX phase, resulting in the MXene sample, extracted from [34].

3 The Influence of Mn-Doping in V_2C MXenes

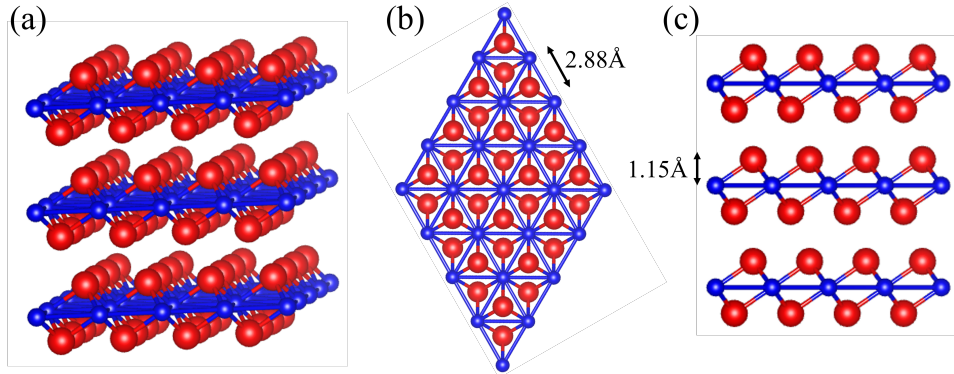


Figure 3.1: Crystallographic structure of V_2C MXene in an overview perspective (a), a top view (b) and a side view (c). Carbon and Vanadium atoms are represented in blue and red, respectively. Extracted from ICSD [12] Coll-Code 5005 and adapted using the software VESTA.

Fig. 3.1 shows the crystallographic structure of V_2C , wherein each layer consists out of three sublayers V-C-V that bond covalently to each other. The MXene structure exhibits a sixfold symmetry and a rhombic unit cell. The stacked conductive layers of MXenes offer fast and easy electron and Li-ion transfer [43] (e.g. Ti_3C_2 MXene exhibits up to 6500 S cm^{-1} [33], which is approx. one order of magnitude less than the electronic conductivity of graphene). Like other MXenes, V_2C thus promises a long cycling stability [43], and a high theoretical capacity of $C_{theo, V_2C} = 470 \text{ mA h g}^{-1}$ (using eq. 2.7, considering two electrons inserted in each structural unit). It is therefore considered as a potential future anode material for LIBs. Aiming to even increase battery performance, doping MXenes was found to be an excellent strategy to manipulate physical and electrochemical properties [44]. In general, a distinction is made between non-metallic and metallic doping. In the past, non-metallic doping of MXenes and the usage as anode materials for LIB applications has already been investigated. As an example, it has been shown that N-doping of Nb_2C increases the interlayer distance and decreases charge transport resistance both by over 50 %, resulting in a significant increase in specific capacity [45]. Although metallic doping was also performed on different MXenes, e.g. Ru-doped Mo_2C or Pt-doped Ti_3C_2 , it was only used in electrocatalysis [46, 47] but not as an anode material for LIB applications. Aiming to investigate the influence of metallic doping of MXenes used as an anode material for LIBs, this work firstly investigates the impact of a Mn doping in V_2C , i.e. Mn- V_2C . The introduction of Mn aims to increase both ionic and electronic conductiv-

ity, to decrease charge transport resistance, as well as to establish another redox reaction center [44]. In this work, both pristine and Mn-doped samples were synthesized by Dr. Peng Guo via pristine V_2AlC and Mn-doped $Mn-V_2AlC$ precursors using a solution of $HCl + LiF$ as an etching solvent.

This chapter characterizes the pristine (V_2C) as well as the Mn-doped ($Mn-V_2C$) MXenes structurally and electrochemically using XRD, SEM, EDS, XPS, CV, GCPL and EIS, thereby elaborating differences in battery performance.

3.1 Physical Characterization

In order to determine the chemical composition and the crystallographic structure of the two powder samples, XRD measurements were performed. Fig. 3.2 shows the XRD pattern of V_2C and $Mn-V_2C$ (both in black). As a reference, the XRD pattern of their precursor materials $Mn-V_2AlC$ (red) and V_2AlC (blue) are plotted. Furthermore, reference patterns of Li_3AlF_6 and LiF are presented in green and pink, respectively. In order to address the origin of the visible peaks inside the diffractograms of the MXenes, their peaks were labelled with markers. The color used, symbolise the phase to which these peaks were attributed. Firstly, red and blue square labels are assigned to diffraction peaks of residual parental MAX phases V_2AlC and $Mn-V_2AlC$, respectively. Secondly, green and pink asterisks labels are assigned to diffraction peaks of Li_3AlF_6 and LiF , respectively. Thus, V_2C features traces of residual MAX phase, Li_3AlF_6 and LiF . In comparison, $Mn-V_2C$ also features traces of residual MAX phase and Li_3AlF_6 . Furthermore, V_2C and $Mn-V_2C$ exhibit a new peak emerging at $2\theta < 10^\circ$, which is assigned to the (002) diffraction peak of pure MXene phase. The (002) peak of the pristine sample is much broader as compared to the Mn-doped sample. The XRD patterns clearly reveal that V_2C and $Mn-V_2C$ consist out of a mixture of several constituting parts, i.e. pure MXene phase, MAX phase, Li_3AlF_6 and LiF .

The dominant diffraction peak related to pure V_2C MXene phase is the (002) diffraction peak occurring in the low angle range [6, 48]. This peak is clearly visible in the XRD patterns of V_2C and $Mn-V_2C$ in Fig. 3.2 and confirms the successful synthesis of MXene phase [49]. The (002) diffraction is attributed to the interlayer spacing of V_2C and $Mn-V_2C$. For both samples, it shifts to lower angles compared to the precursor materials, indicating a widening of the interlayer spacing and the successful exfoliation of the Al layer [34, 49]. While the (002) reflex of the pristine MXene occurs at $2\theta = 8.67(15)^\circ$, the reflex of the Mn-doped sample is at slightly lower angles at $2\theta = 7.78(1)^\circ$ (both highlighted with vertical dashed lines), which indicates different interlayer spacings. Using Bragg's law (see eq. 2.1), the interlayer spacings were extracted, the results are listed in table 3.1.

$Mn-V_2C$ MXene exhibits a $> 10\%$ enlarged interlayer spacing compared to V_2C . The difference might arise from higher ionic radii of Mn compared to V, which might further open and widen the layers. Since ionic radii depend on the oxidation states of the species [50], this possible explanation will be discussed in following XP spectra. As indicated in the XRD pattern of V_2C and $Mn-V_2C$ in Fig. 3.2, the (002) diffraction peak is clearly

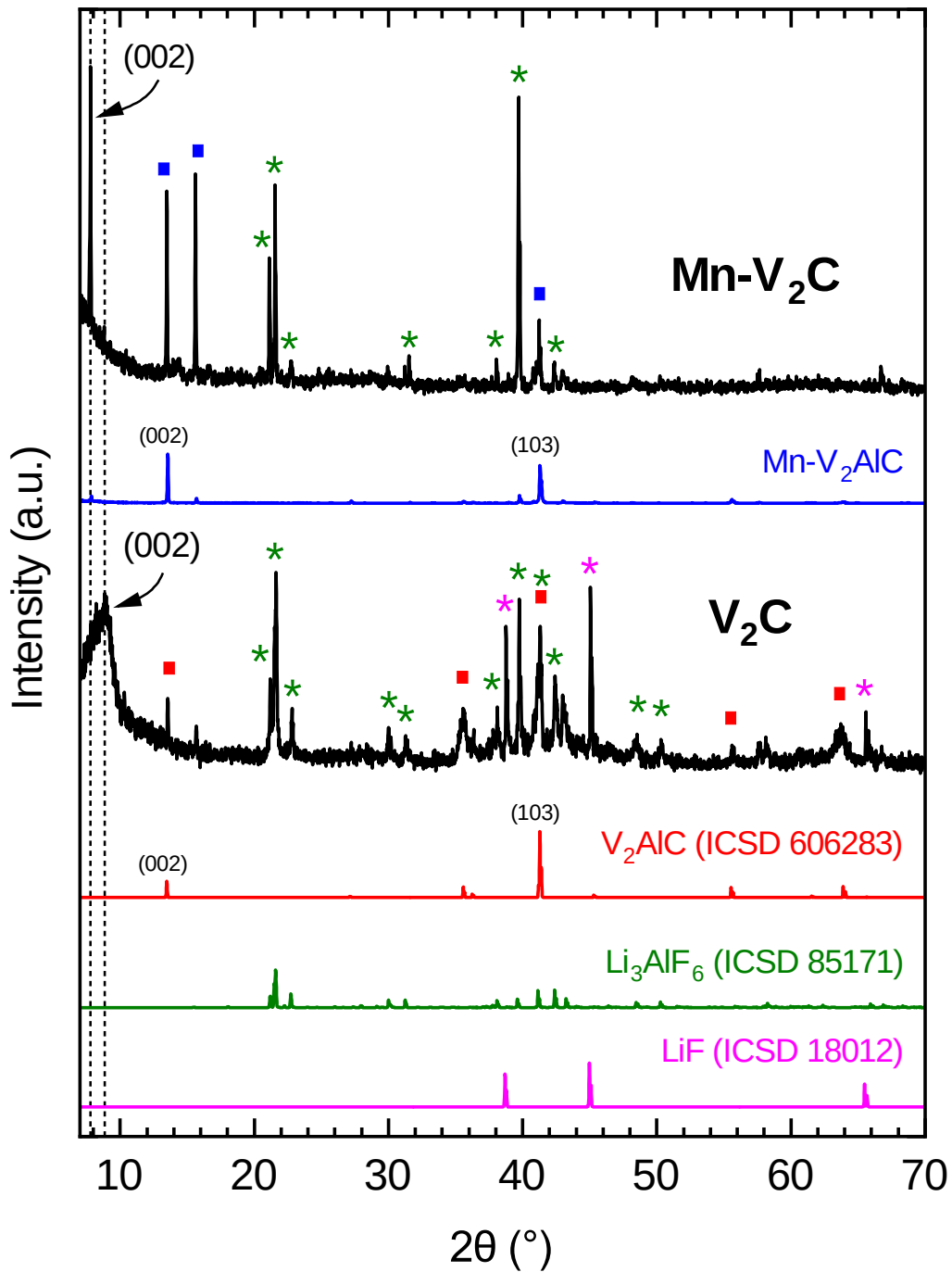
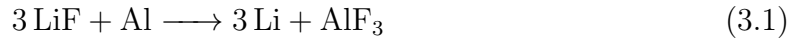


Figure 3.2: XRD patterns of Mn- V_2C and V_2C (both black) together with reference patterns of the precursor materials Mn- V_2AlC (blue) and V_2AlC (red, [12] Coll. Code 606283), as well as impurity phases Li_3AlF_6 (green, [12] Coll. Code 85171) and LiF (pink, [12] Coll. Code 18012). Labels on the Mn- V_2C and V_2C patterns represented as blue and red squares are associated with the precursor materials, green and pink asterisks are related to impurity phases. The (002) diffraction peak of Mn- V_2C and V_2C is highlighted with dashed black lines.

Table 3.1: Extracted 2θ values of the (002) diffraction peaks of V_2C and $Mn-V_2C$ as well as their precursors from the XRD pattern in Fig.3.2 and corresponding calculated interlayer distances c .

Sample	$2\theta(^{\circ})$	$c(\text{\AA})$
V_2AlC	13.49(3)	5.12(1)
V_2C	8.67(15)	6.38(11)
$Mn-V_2AlC$	13.49(4)	5.12(2)
$Mn-V_2C$	7.78(3)	6.74(3)

not the only observed peak, both samples are very impure. As described above, in V_2C , traces of residual V_2AlC MAX phase as well as LiF and Li_3AlF_6 are identified. $Mn-V_2C$ features traces of residual $Mn-V_2AlC$ MAX phase and Li_3AlF_6 . Li_3AlF_6 was introduced during the synthesis via the following reaction processes:



Here, the Al from the A phase of the precursor reacts with LiF of the etching solvent, resulting in AlF_3 . This reacts again with LiF to Li_3AlF_6 . The formation of these impurities during MXene synthesis also occurred in literature [9, 51], but MXene synthesis without mayor impurities was proven to also be possible [36, 37]. Since there is only one mayor peak associated to pure MXene phase [34] and some peaks may originate from more than one impurity phase, the exact weight contribution of these different phases could not be extracted. All in all, the XRD pattern in Fig. 3.2 reveal that V_2C and $Mn-V_2C$ consist out of three constituting parts, i.e. pure MXene phase, residual MAX phase and impurity phases. The fact that the two samples are phase impure makes it more difficult to investigate on the impact of Mn-doping in V_2C MXenes.

To investigate the morphology of the pristine and the Mn-doped MXenes, SEM measurements were performed. Fig. 3.3 shows SEM images of (a) $Mn-V_2AlC$ before the synthesis, as well as (b) $Mn-V_2C$ and (c) V_2C after the synthesis. The precursor material in Fig. 3.3(a) displays densely packed particles in the range of several micrometers. $Mn-V_2C$ and V_2C in Fig. 3.3(b-c) display the same morphology of several micrometer sized particles with an open accordion-like structure and a lot of void space.

The SEM measurements in Fig. 3.3 reveal that the applied synthesis leads to a drastic morphological change, from a solid bulk structure to an open accordion-like structure. This change in morphology is typical for MXenes and confirms the successful exfoliation of the Al phase [6, 52, 53]. The open lamella morphology thereby originates from the outfanning of the planes because of the insertion of surface functional groups like H , O , HO and/or F into the etched interlayer sites [6]. This structure offers adequate channels for electrolyte penetration and shortens the migration pathway for Li -ions [54, 55]. The layers

of this accordion-like structure thereby do not directly display the exfoliated Al layers, which occur in a whole different length scale. While from XRD, the interlayer spacing was determined to be in the Ångström range, the SEM resolution is limited to the low micrometer range. In direct comparison, V_2C and $Mn-V_2C$ feature the same morphology. The exact amount of Mn-doping was measured using EDS. $Mn-V_2C$ features only 0.76(42) % of Mn, which is too little amount to expect a significant morphology change.

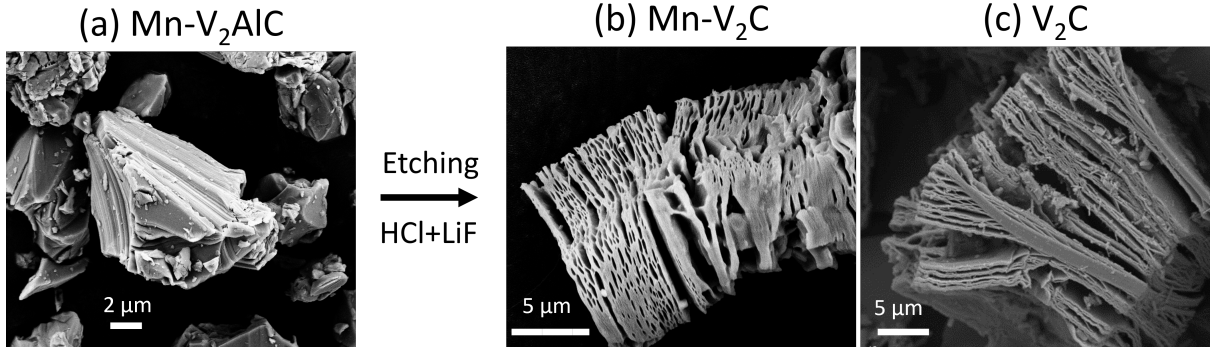


Figure 3.3: SEM images of (a) $Mn-V_2AlC$ precursor material, (b) $Mn-V_2C$ MXene and (c) V_2C MXene. (a) and (b) were measured by the author, (c) was measured by Dr. Peng Guo.

In order to determine the elemental distribution as well as the oxidation states of V_2C and $Mn-V_2C$, XP spectra were recorded by Prof. Dr. Michael Zharnikov at the Institute of Applied Physical Chemistry at Heidelberg University. In every subfigure of XPS data in Fig. 3.4 an intensity signal is plotted over the binding energy. Fig. 3.4 shows (a) survey spectra from 0 to 700 eV of the pristine and Mn-doped MXenes in blue and red, respectively. In the pristine MXene, all mayor expected elements (V, C, F, Al, and O) were identified. The survey spectra of the Mn-doped MXene looks very similar with the same identified elements. Furthermore, a weak expected Mn peak was observed. In the survey spectrum of V_2C in Fig. 3.4(a), V2p and C1s state signals could indicate the existence of pure MXene phase. The existence of Al2p state signals likely show the existence of residual MAX phase. The existence of F1s state and F_{KLL} Auger peak signals show the existence of F that was introduced during the etching process. Combined with the occurrence of Al, this could also indicate the existence of the Li_3AlF_6 impurity. However, Li could not be identified probably due to its extremely low characteristic sensitivity factors [56]. O1s state signals arise most probably from absorbed O on the sample, while it was exposed to normal atmosphere. As described above, the survey spectrum of $Mn-V_2C$ looks very similar with the same elemental composition. In addition, it features a weak Mn2p state signal due to the light Mn-doping. All in all, the XP survey spectrum of $Mn-V_2C$ and V_2C in Fig. 3.4(a) is in good consensus with XRD pattern in Fig. 3.2.

Fig. 3.4(b) shows the V2p state core level spectrum. V_2C features two broad peaks at 523.2 eV and 516.2 eV, each exhibiting a right shoulder at 521.2 eV and 513.2 eV. $Mn-V_2C$ exhibits very similar data, while the aforementioned shoulders are more pronounced as distinct, independent peaks. In the V2p spectrum of V_2C , the two main peaks at 523.2 eV

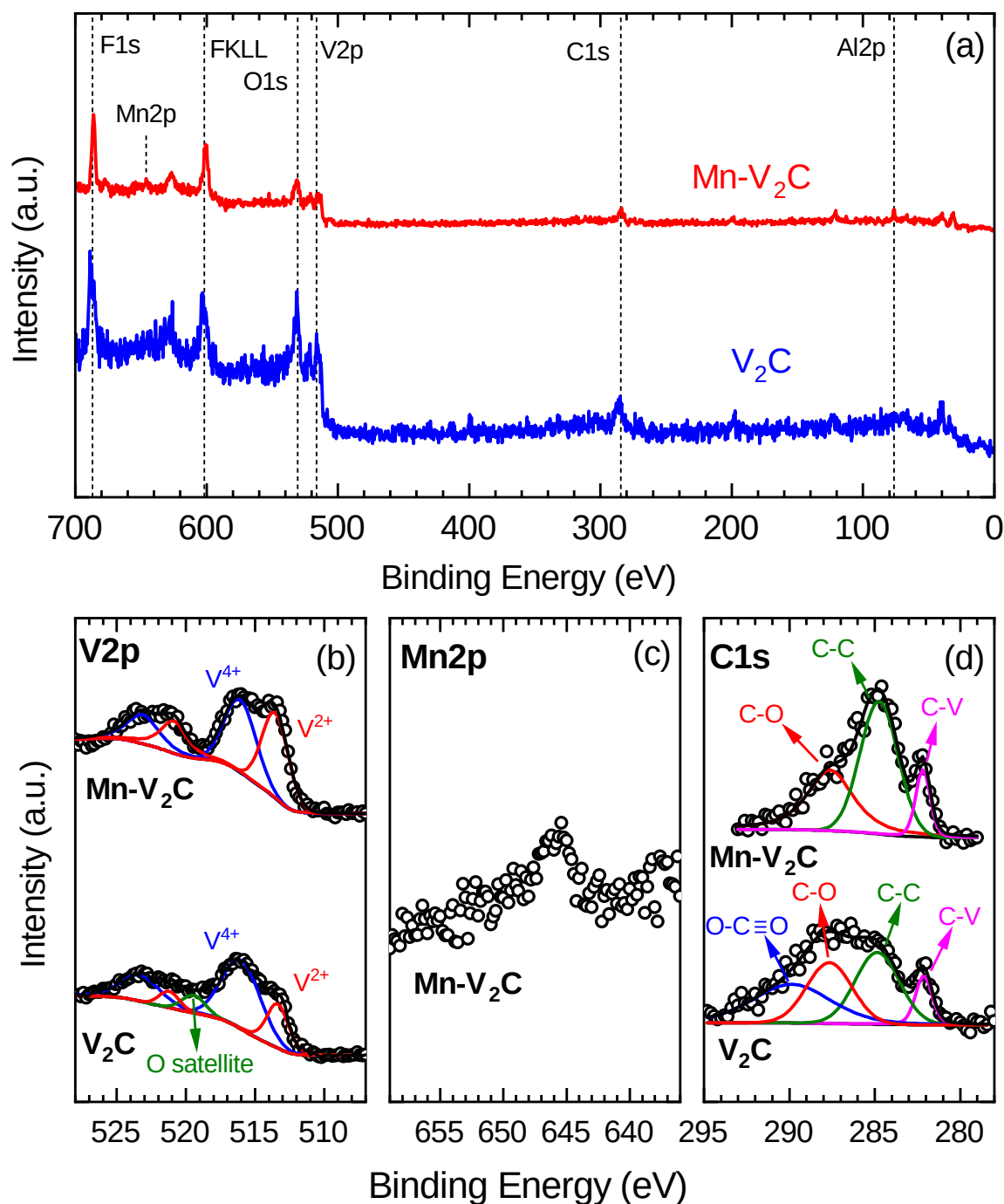


Figure 3.4: XPS spectra of Mn-V₂C and V₂C. (a) shows survey spectra with vertical dashed lines as markers of the main constituting elements. (b-d) show core level spectra of V2p, Mn2p and C1s states, respectively. The lines display fits according to the presumed spectral contribution. XP spectra were recorded and fitted by Prof. Dr. Michael Zharnikov at the Institute of Applied Physical Chemistry at Heidelberg University.

and 516.2 eV correspond to the V^{4+} doublet state (fitted in blue) [18]. The two right shoulders at 521.2 eV and 513.2 eV suggest the existence of another doublet state, which is assigned to the V^{2+} doublet state (fitted in red) [18]. Thus, V in V_2C is oxidized as V^{4+} and V^{2+} . The intensity differences between V^{4+} and V^{2+} suggest a higher abundance of V^{4+} . Furthermore, the signal at around 519.4 eV between the two doublet states does not decrease significantly, which suggests the existence of another peak, assigned to an O satellite peak [18] of unknown origin. Mn- V_2C exhibits similar behavior like V_2C . The two observed doublet states correspond to V^{4+} and V^{2+} oxidation states. The only differences are the higher intensity of V^{2+} suggesting a higher abundance, and the absence of the O satellite peak observed in V_2C . Due to the occurrence of two V oxidation states, it cannot be determined, whether V^{2+} and/or V^{4+} are reduced during cycling in electrochemical measurements. Ex-situ XPS performed after cell discharge would give this information.

Fig. 3.4(c) shows the Mn2p state core level spectrum. Mn- V_2C features a very noisy signal with a main peak at 645.4 eV. The existence of only a single peak, even though the expected Mn^{4+}/Mn^{2+} are doublet states [18] is intriguing. The reason for a missing second peak is likely that it is hidden due to the low Mn-amount of 0.76(42) % in the sample. Consequently, it cannot be determined, which element exhibits higher ionic radii. For that reason, the hypothesis, that the difference in interlayer spacing between V_2C and Mn- V_2C (observed in XRD in Fig. 3.2) originates from different ionic radii of V and Mn can neither be confirmed nor denied. V_2C was not plotted in the Mn2p state spectrum since there is no Mn signal expected.

Fig. 3.4(d) shows the C1s state core level spectrum. V_2C features a broad peak at 286.4 eV, and a peak at 282 eV. In comparison, Mn- V_2C also exhibits the peak at 282 eV and a sharper peak at 284.6 eV with a left shoulder at 287.8 eV. In the C1s state spectrum of V_2C , the broad peak at 286.4 eV and the peak at 282 eV reveal the overlapping coexistence of four different peaks at 290 eV, 287.6 eV, 284.8 eV and 282 eV. These correspond to chemical bonds $O-C\equiv O$ (blue), $C-O$ (red), $C-C$ (green) and $C-V$ (pink), respectively [18]. In comparison, the Mn-doped sample exhibits again similar behavior. It reveals the coexistence of the same bonding, except $O-C\equiv O$, which is missing.

3.2 Electrochemical Characterization

In order to investigate the electrochemical activity of the MXenes, CV, GCPL and EIS measurement were performed and will be discussed in the following. As discussed in chapter 3.1, V_2C and Mn- V_2C do not only consist out of pure MXene phase but also out of other constituting parts, like residual MAX phase and impurity phases. Thus the electrochemical activities of these other parts will be considered first.

Fig. 3.5 shows CV and GCPL measurements of Mn- V_2AlC . Fig. 3.5(a) shows a cyclic voltammogram of Mn- V_2AlC at a scan rate of 0.1 mV s^{-1} . During the first discharge scan (in black), two reduction peaks are observable at $R_{SEI} = 0.64 \text{ V}$ and $R_{C2} = 0.01 \text{ V}$. During the first charge scan, two oxidation peaks are observable at $O_{C2} = 0.13 \text{ V}$ and

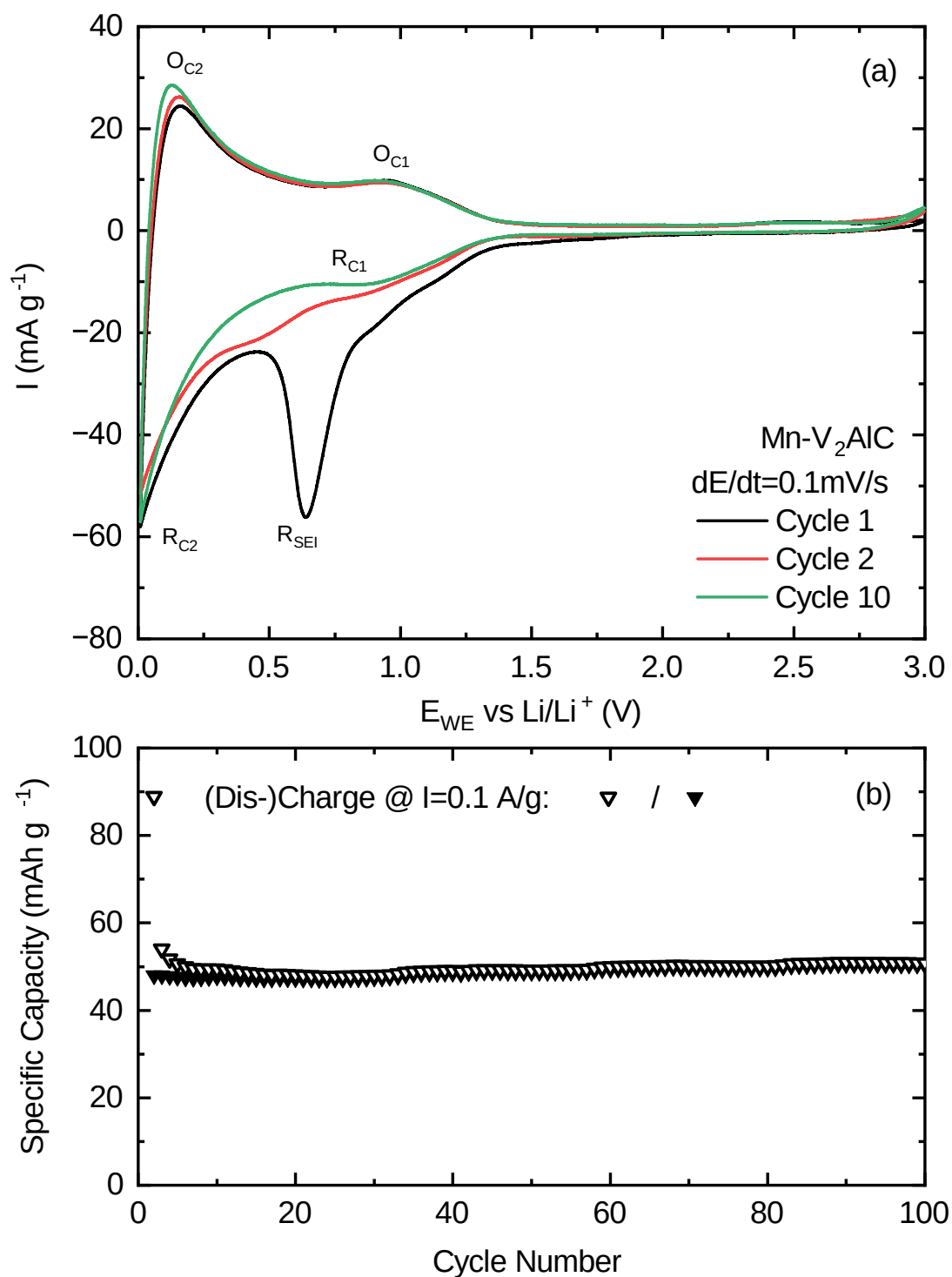


Figure 3.5: CV and GCPL measurements of Mn- V_2AlC . (a) shows a CV of cycle 1, 2 and 10 (in black, red and green, respectively) measured at a scan rate of 0.1 mV s^{-1} . The labels R/O represent distinct reduction and oxidation peaks. (b) shows specific discharge and charge capacities at 0.1 A g^{-1} obtained in the voltage regime from 0.01 to 3 V.

$O_{C1} = 0.96$ V. In the second and 10th discharge scan (in red and green respectively), only the reduction peak R_{C2} , as well as a new peak at $R_{C1} = 0.81$ V are present. The second and 10th charge scan feature the same peaks which were already observed in the first charge scan. The vanishing of R_{SEI} after the first cycle indicates irreversible behavior and is assigned to SEI formation [30, 31]. The other peaks are identified as redox pairs. R_{C1}/O_{C1} and R_{C2}/O_{C2} are redox processes clearly related to the intercalation of Li-ions into CB (compare with chapter 2.4 Fig. 2.5). The CV of the Mn- V_2C electrode is thus dominated by CB contributions. In order to evaluate the contribution of the Mn- V_2C precursor in specific capacity, GCPL measurements were performed. Fig. 3.5(b) shows specific capacities of Mn- V_2C at a (dis-)charging current of 0.1 A g^{-1} over the first 100 cycles. The initial specific capacity of 89 mA h g^{-1} drops after the first cycle and saturates quickly to 50 mA h g^{-1} . Subtracting the 45 mA h g^{-1} in specific capacity contribution originating from 20 % weight proportion of CB in the working electrode, results in a final specific capacity of $\sim 5 \text{ mA h g}^{-1}$. This value is assigned as contribution of Mn- V_2AlC precursor and is almost negligible. All in all, results from Fig. 3.5 reveal, that also the MAX phase is almost electrochemically inactive. Li_3AlF_6 is used as electrolyte [57, 58] and is therefore inactive in the potential window from 0.01 to 3 V. Nevertheless, Li_3AlF_6 and residual MAX phase contribute to V_2C and Mn- V_2C by weight.

The above results show that impurities observed in the XRD pattern of V_2C and Mn- V_2C are electrochemically inactive. Thus, the redox activities of the MXenes will now be investigated. Fig. 3.6 shows cyclic voltammograms (CV) of (a) V_2C and (b) Mn- V_2C measured at a scan rate of 0.1 mV s^{-1} . Both samples reveal several irreversible and reversible reduction and oxidation peaks, which will be described and discussed in the following. The CV of V_2C in Fig. 3.6(a) exhibits several reduction peaks during the first discharge scan (indicated in black) at $R^* = 2.85$ V, $R^{**} = 2.48$ V, $R_1 = 1.73$ V, $R_2 = 0.98$ V, $R_{SEI} = 0.67$ V and $R_C = 0.01$ V. During the first charge scan, several oxidation peaks at $O_C = 0.24$ V, $O_3 = 0.87$ V, $O_2 = 1.23$ V and $O_1 = 2.61$ V are observable. In the third and 10th discharge scan (indicated in red and green, respectively) only the reduction peaks at R_1 , R_2 and R_C , as well as a new peak at $R_3 = 0.58$ V are present. The third and 10th charge scan features the same peaks which were already observed in the first charge scan with a slight decrease in intensity. In comparison, the CV of Mn- V_2C MXene in Fig. 3.6(b) exhibits a very similar behavior with the same oxidation and reduction peaks in the first, third and 10th cycle. The only difference is a new oxidation peak is occurring at $O_{new} = 1.76$ V, while no new reduction peak could be observed.

In the CV of V_2C in Fig. 3.6(a), the vanishing of the peaks R^* , R^{**} and R_{SEI} after the first cycle indicate irreversible behavior. The origin of R^* and R^{**} is unclear. In literature about V_2C MXene these peaks are not displayed, leading to the conclusion that they probably originate from a irreversible reaction of some minor impurity phase. R_{SEI} can be unambiguously assigned to the formation of the solid electrolyte interfacial layer (SEI) [30, 31]. All other reduction and oxidation peaks are reversible and are identified as redox pairs. R_C/O_C are assigned to the intercalation of Li-ions into electrochemically active Carbon black (CB) which is a constituent of the electrode (compare with chapter 2.4, Fig. 2.5). Furthermore, three redox pairs at R_1/O_1 , R_2/O_2 and R_3/O_3 can be assigned

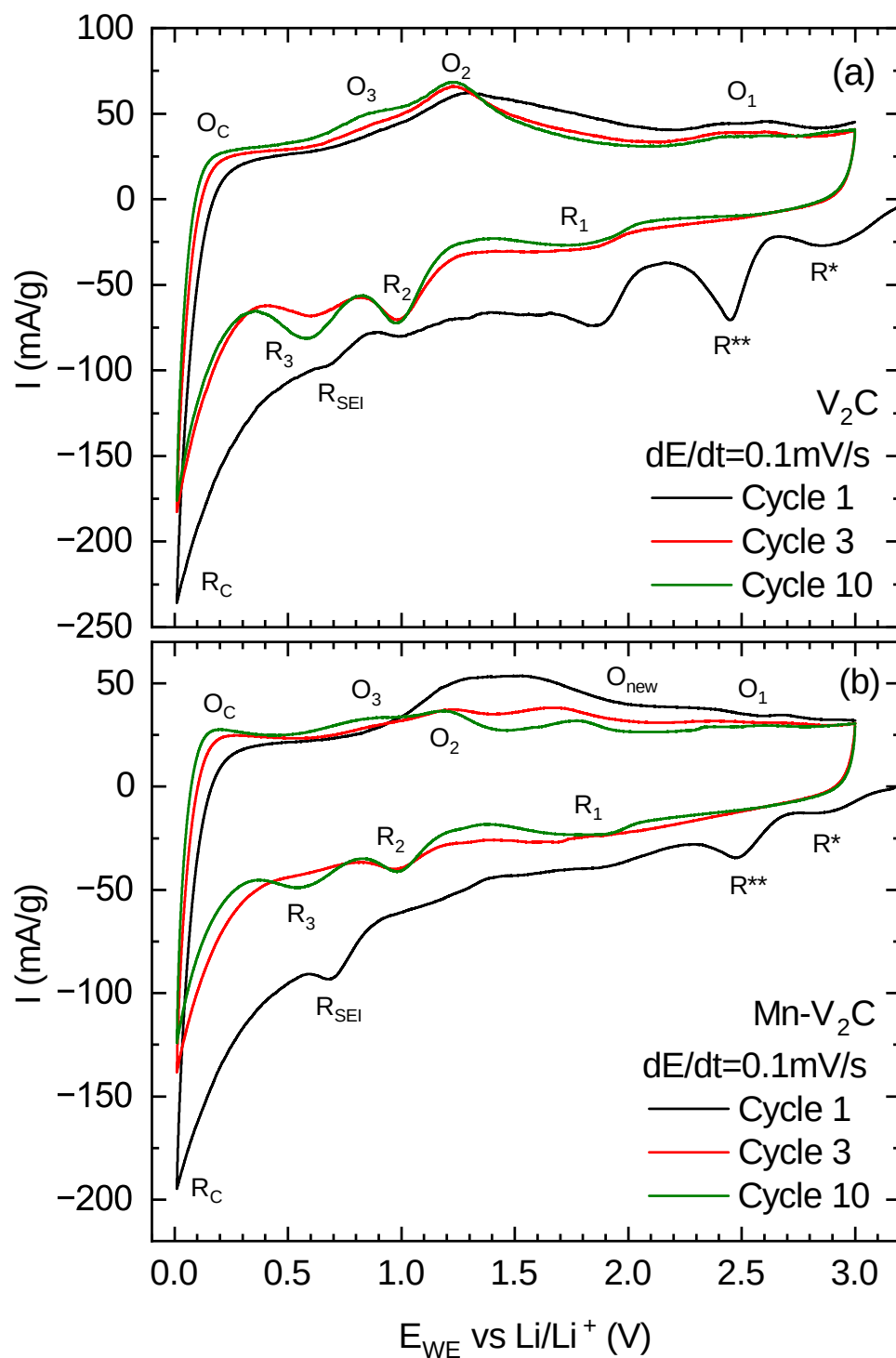
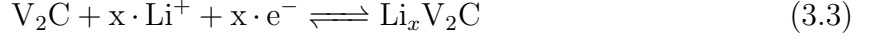


Figure 3.6: Cyclic voltammograms of cycle 1, 3 and 10 of (a) V_2C and (b) $Mn-V_2C$ measured at a scan rate of 0.1 mV s^{-1} . The labels R/O represent distinct reduction and oxidation peaks.

to Li-ions intercalating into the active material, in agreement with literature data [9, 10]. The intercalation process taking place is given as follows:



In comparison, the CV of Mn- V_2C shown in Fig. 3.6(b) features a very similar behavior. It also exhibits the irreversible reduction processes R^* , R^{**} and SEI formation R_{SEI} , as well as the redox pairs R_C/O_C assigned to Carbon black. Moreover the three redox pairs $R_{1,2,3}/O_{1,2,3}$ are also observable. The origin of the new oxidation peak O_{new} is unknown. Since no corresponding reduction peak is observed, the peak is probably not related to redox reactions of Mn. Furthermore, $\sim 1\%$ of Mn-doping is a too little weight contribution to obtain such a strong oxidation peak. It is also possible, that O_2 split to two oxidation peaks of lower intensity. The discussion about this new peak will be taken up again when discussing the potential profiles of the MXenes.

To evaluate the overall performance of the two samples, GCPL measurements were performed. Fig. 3.7 shows specific capacities of V_2C (blue) and Mn- V_2C (red) at different current densities over specific cycling ranges. Fig. 3.7(a) shows the specific capacities at a (dis-)charging current of $I = 0.1 \text{ A g}^{-1}$ over the first 150 cycles. V_2C (blue) exhibits an initial capacity of 393 mA h g^{-1} , which drops to 218 mA h g^{-1} and then gradually increases and saturates at 257 mA h g^{-1} at cycle 150. The specific capacity of Mn- V_2C (red) shows a similar behavior. It features an initial capacity of 614 mA h g^{-1} which drops after the first cycles to 253 mA h g^{-1} and then increases up to 335 mA h g^{-1} . Fig. 3.7(b) shows the specific capacities at a higher (dis-) charging current of $I = 1 \text{ A g}^{-1}$ over 2000 cycles. The initial capacity of Mn- V_2C (blue) of 184 mA h g^{-1} drops after the first cycle and saturates quickly to 65 mA h g^{-1} . Again, the specific capacity of Mn- V_2C (red) shows a similar behavior. The initial capacity of 254 mA h g^{-1} drops after the first cycle and saturates at 100 mA h g^{-1} . Subjecting a gradual capacity fading, Mn- V_2C exhibits 90 mA h g^{-1} after 2000 cycles with an almost perfect Coulomb efficiency (light red) of $> 99\%$. Upon cycling, sinusoidal oscillations in the capacity measurements were recorded in both samples. Fig. 3.7(a-b) clearly reveal increased specific capacities of Mn- V_2C compared to V_2C both at low and at high current densities over long cycling ranges. In the following, these results will be discussed in detail.

In GCPL measurements in Fig. 3.7(a) of V_2C (blue), the fading in specific capacity after the first cycle can be assigned to SEI formation [30, 31] and irreversible processes, as observed in the CV in Fig. 3.6(a). Subsequent continuous (dis-)charging result in volume changes of the active material due to (de-)lithiation, which changes the crystallinity and affects the diffusion coefficient, resulting in an capacity increase due to the activation of the material [59]. The capacity value of 257 mA h g^{-1} of V_2C after 150 cycles corresponds to approx. 0.89 electrons intercalated in each structural unit in V_2C (contribution of CB to the specific capacity was subtracted). Table 3.2 compares the specific capacity value of V_2C in this work with the theoretical capacity and literature values. The theoretical capacity of V_2C was calculated to be $C_{theo,V_2C} = 470 \text{ mA h g}^{-1}$, considering two electrons intercalated in each structural unit. The discrepancy of 2 electrons compared to 0.89 electrons inserted in each structural unit as measured, might originate from impurities in

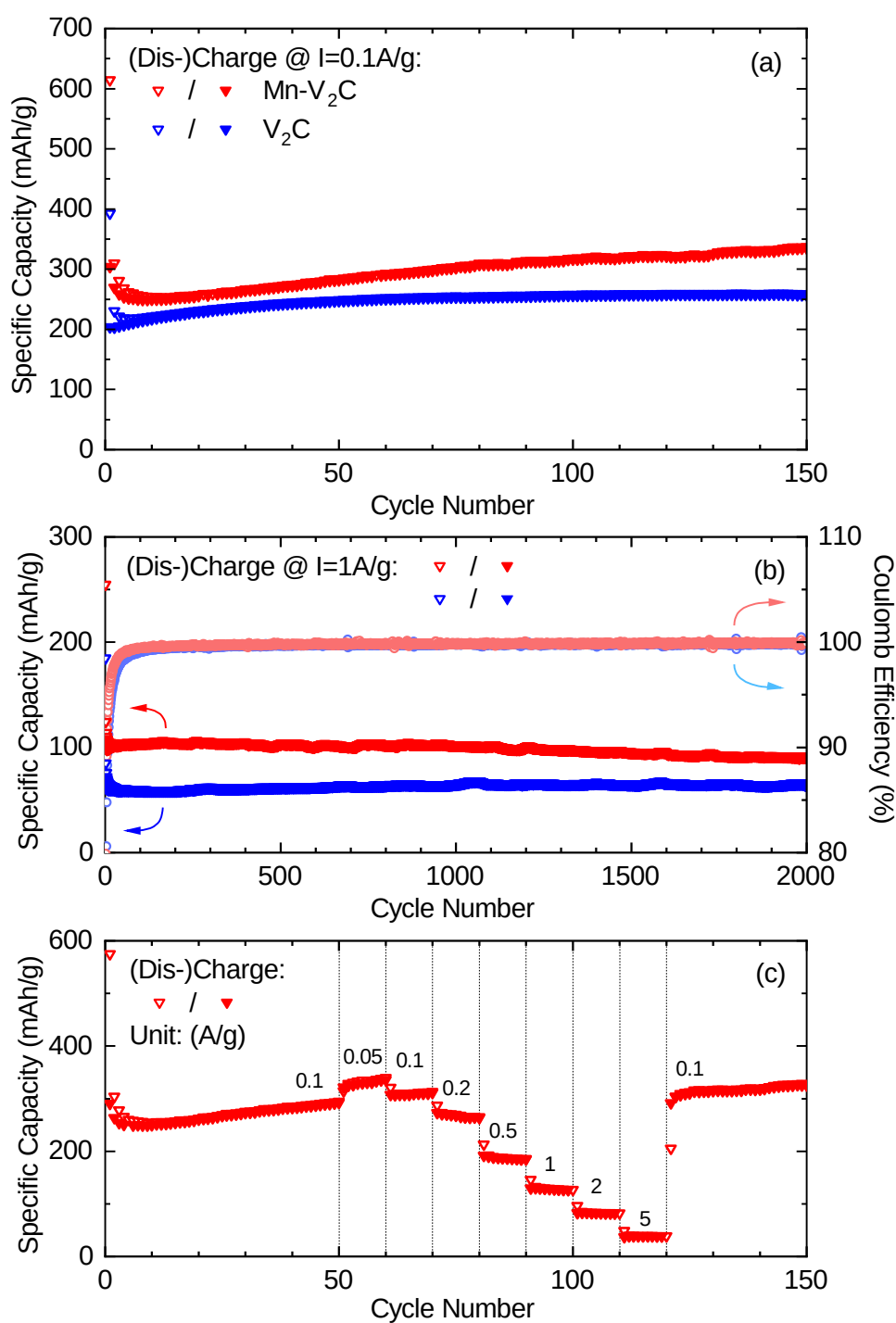


Figure 3.7: (a) Specific discharge and charge capacities of V_2C (blue) and $Mn-V_2C$ (red) electrodes at 100 mA g^{-1} obtained in the voltage regime from 0.01 to 3 V. (b) Long-term cycling performance of V_2C (blue) and $Mn-V_2C$ (red) electrodes at 1 A g^{-1} up to 2000 cycles and corresponding Coulomb efficiencies in light blue and light green, respectively. (c) Rate capacities of the $Mn-V_2C$ electrode at different current densities between 0.05 and 5 A g^{-1} .

Table 3.2: The total specific capacity values after cycle 100 at a (dis-)charging current of 0.1 A g^{-1} and corresponding amount of inserted electrons per structural unit in V_2C MXenes. The mass ratio of active material (AM), Carbon black (CB) and binder (PVDF) of the electrode is also indicated. The mass contribution of CB to the specific capacity was subtracted before calculating the amount of inserted electrons per structural unit. The values are compared to theory and literature.

Source	Capacity (mAh/g)	AM:CB:PVDF	# Electrons
Theory	470	/	2
This Work	256	70:20:10	0.89
[9]	190(10)	70:20:10	0.62(4)
[10]	200(10)	80:10:10	0.75(4)
[11]	260	80:10:10	1.01

the sample. Residual MAX phase as well as Li_3AlF_6 are observed via XRD in Fig. 3.2. As discussed in chapter 3.1, these phases are electrochemically inactive but still have mass contributions, which decreases the effective specific capacity. Nevertheless, the capacity obtained in this work is well comparable with literature. While [9, 10] show lower specific capacities at same current densities, [11] exhibits a light higher value at a higher current density.

In direct comparison, the specific capacity of $\text{Mn}-V_2C$ (red) exhibits a similar behavior and outperforms V_2C over the whole cycling range. After 150 cycles, the specific capacity of $\text{Mn}-V_2C$ exceeds the capacity of V_2C by more than 30 %. This increased performance is also observed at higher current densities, as shown in Fig. 3.7(b), thereby demonstrating excellent cycling stability with almost no losses after 2000 cycles and an almost perfect Coulomb efficiency of $> 99 \%$. Sinusoidal instabilities during cycling can be assigned to problems with the temperature control on the measuring setup during cycling. Altering temperatures have a significant impact on the specific capacity of LIB [60].

Fig. 3.7(c) shows rate performance measurements of $\text{Mn}-V_2C$ at varying current densities between 0.05 and 5 A g^{-1} upon cycling. Cycling started at 0.1 A g^{-1} up to cycle 50, then gradually decreases to 0.05 A g^{-1} and increases to 5 A g^{-1} in steps of 10 cycles each. Finally, the current density decreases again to 0.1 A g^{-1} . In the first 50 cycles the capacity features a similar behavior like in Fig. 3.7(a). Upon altering the current density, the capacity increased with lower and decreased with higher currents. At a current increase by one order of magnitude from 0.1 A g^{-1} to 1 A g^{-1} , the specific capacity undergoes a capacity retention of approx. 65 %. When decreasing the current density back to the initial 0.1 A g^{-1} , the specific capacity increases to the initial value. There are several reasons for capacity losses. First, irreversible heat dissipation causes power losses. Second, fast charging might be restricted to the resistance of the electrodes. Third, so-called Li-plating might occur, in which Li-ions, instead of intercalating into the active material of the anode,

rather accumulate as metallic Li on the surface of the electrode. This unwanted reaction occurs when the potential of the negative electrode drops below the Li/Li^+ redox potential [61]. All in all, the results from Fig. 3.7 show the high reversibility of the intercalation processes.

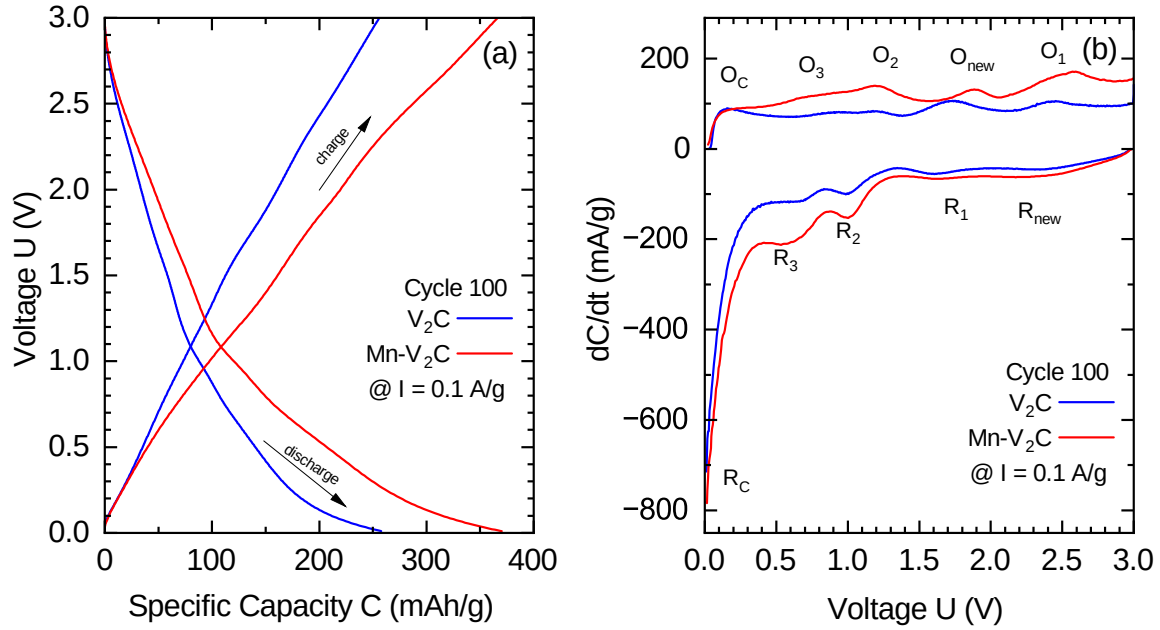


Figure 3.8: (a) GCPL potential profiles of cycle 100 of V_2C (blue) and $Mn-V_2C$ (red) at 0.1 A g^{-1} . (b) Time derivatives of inverse potential profiles from (a).

In order to assess the origin for the difference in specific capacity between V_2C and $Mn-V_2C$, Fig. 3.8 shows their GCPL potential profiles of cycle 100 at a current density of 0.1 A g^{-1} and its inverse time derivatives. Fig. 3.8(a) shows the potential profiles of V_2C (blue) and $Mn-V_2C$ (red). Plotted is the voltage of the working electrode over the specific capacity. Both samples feature an almost linear behavior with small variations. As already demonstrated in Fig. 3.7(a), the Mn-doped sample exhibits a higher specific capacity, which is also visible here. In order to elaborate differences of these two profiles easier, the time derivative of the inverse of the potential profile dC/dt was calculated and displayed in Fig. 3.8(b). Plotted is the time derivative dC/dt over the voltage of the working electrode. In both samples, several peaks become visible, that were already observed in the CVs in Fig. 3.6. These are the redox pairs R_C/O_C , $R_{1,2,3}/O_{1,2,3}$ and the new emerging oxidation peak O_{new} . Furthermore, another reduction peak is visible at $R_{new} = 2.21 \text{ V}$. Both new peaks do not only occur in the Mn-doped but also in the pristine sample. The reduction and oxidation peaks $R_{1,2,3,new}/O_{1,2,3,new}$ are significantly more pronounced in $Mn-V_2C$ compared to V_2C . The derivative of the potential profiles clearly reveal that same redox processes and no new processes are taking place in both samples.

The GCPL potential profiles of V_2C (blue) and $Mn-V_2C$ as well as its time derivatives in Fig. 3.8(a-b) suggest different redox pairings as extracted from CV. Redox reactions

in which the reduction occurs at a higher voltage than the corresponding oxidation is electrochemically forbidden [23], which leads to the new redox pairing of R_{new}/O_1 and R_1/O_{new} . This contradicts to CV measurements in Fig. 3.6. The peak intensities of R_C/O_C corresponding to intercalation processes of Li-ions into CB are of the same order of magnitude for both samples, indicating that their contribution to the specific capacity is the same. This is reasonable, since both samples have the same amount of CB weight contribution of 20 %. Since R_{new} and O_{new} occur in both the pristine and the Mn-doped MXenes, this shows that their origin is not related to the introduction of Mn. $\sim 1\%$ Mn-doping does not alter electrochemical processes taking place in V_2C MXenes. Thus, the difference in battery performance between V_2C and Mn- V_2C is not related to an emerging Mn redox reaction center. A possible alternative explanation are the different constituting phases, as observed in XRD in Fig. 3.2. Different mass proportions of the constituents of the samples, i.e. pure MXene phase, residual MAX phase and impurity phases, may lead to different specific capacities. For instance, V_2C could feature more electrochemically inactive residual precursor material and impurity phase compared to Mn- V_2C , resulting in a decreased specific capacity. Nevertheless, another explanation for the difference in battery performance is related to the increased interlayer distance due to the Mn-doping. An increased interlayer spacing of Mn- V_2C compared to V_2C can increase Li-ion transport properties and lead to faster kinetics [62]. This effect was already observed in N-doping of Nb_2C MXenes [45], resulting in a significant increase in specific capacity.

In order to evaluate the kinetics and the supposed differences in charge transport properties of the MXenes, EIS measurements were performed. Fig. 3.9 shows a Nyquist plot of V_2C (blue) and Mn- V_2C (red) after OCV. Both samples feature three regimes. The first regime is an offset on the x-axis in the high frequency range, which corresponds to the bulk resistance of the cell. The second regime displays a semicircle behavior in the high to medium frequency range and is related to the charge transport resistance. Mn- V_2C thereby features a decreased half circle diameter compared to V_2C . The third linear regime in the low frequency range indicates the diffusion impedance. An equivalent circuit shown in the inset of Fig. 3.9 is used to fit the first and second regime. It consists out of a resistance R_1 connected in series with a resistance R_2 and a capacitance C_2 that are connected in parallel. Their values are given in table 3.3.

In the first regime, the values of the bulk resistances R_1 and thus Ohmic resistances of the pristine and the Mn-doped MXenes are almost identical with $1.2(2)\Omega$ and $1.3(1)\Omega$, respectively. In the second regime, both samples feature a half circle behavior with different radii. While in V_2C the charge transport resistance R_2 is at $73(1)\Omega$ and double layer capacity C_2 at $2.1(1)\mu F$, the Mn-doped sample exhibits lower values of $52.7(3)\Omega$ and $3.7(2)\mu F$, clearly demonstrating a decreased charge transport resistance by $\sim 28\%$. The increased specific capacity and superior high current capability of Mn- V_2C observed in Fig. 3.7(a-b) in combination with a significantly decreased charge transport resistance conclude enhanced kinetics of Mn- V_2C over V_2C . This result adds up to the changed interlayer spacing and may also be a reason for a $> 30\%$ increased specific capacity of Mn- V_2C over V_2C .

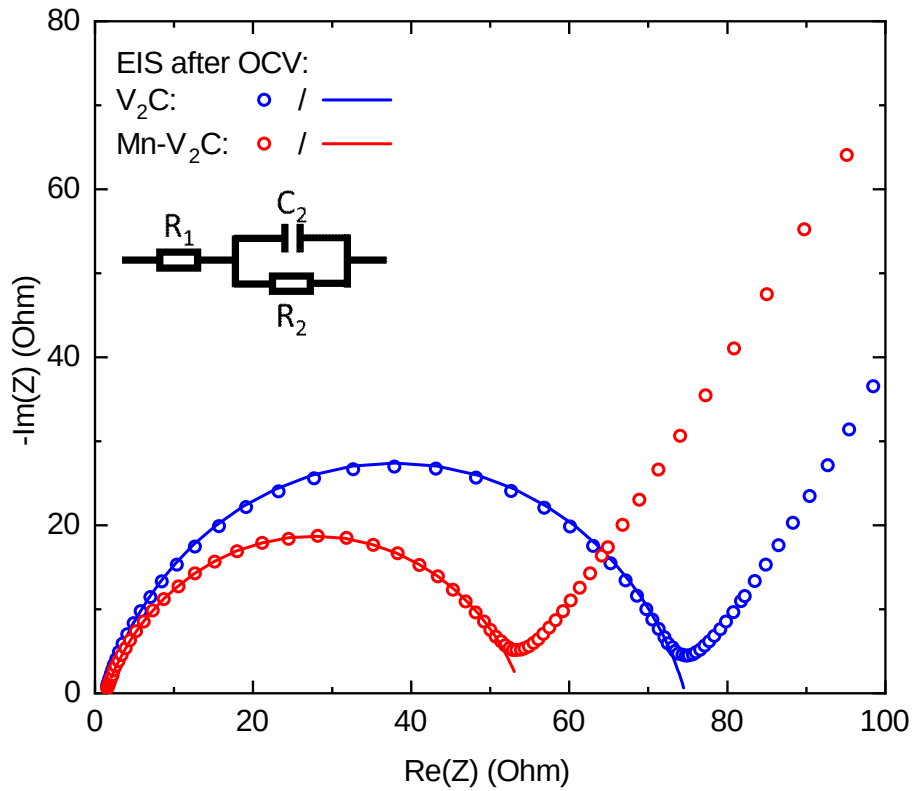


Figure 3.9: Nyquist plot of impedance measurements on V_2C (blue) and $Mn-V_2C$ (red) after OCV. Solid lines represent fits of the equivalent circuit shown in the inset.

Table 3.3: Extracted values of the EIS equivalent circuit elements R_1 , R_2 and C_2 used for the EIS fit of V_2C and $Mn-V_2C$. The error values were extracted by altering the fitting parameters to an insufficient fit.

Sample	$R_1(\Omega)$	$R_2(\Omega)$	$C_2(\mu F)$
V_2C	1.2(2)	73(1)	2.1(1)
$Mn-V_2C$	1.3(1)	52.7(3)	3.7(2)

3.3 Conclusion for Mn-Doping in V_2C

This work investigated the impact of $\sim 1\%$ Mn-doping on V_2C MXenes, i.e. Mn- V_2C using several physical and electrochemical characterization methods. Dr. Peng Guo synthesized the samples V_2C and Mn- V_2C via the precursor materials V_2AlC and Mn-doped V_2AlC by selectively etching the Al phase using a solution of $HCl + LiF$ as an etching solvent. Both MXenes (V_2C and Mn- V_2C) exhibit an emerging (002) diffraction peak at $2\theta < 10^\circ$ in XRD measurements, which demonstrates an increased interlayer distance compared to the precursor materials and confirms the successful synthesis of pure MXene phase. In comparison to V_2C , Mn- V_2C thereby exhibits a $> 10\%$ increased interlayer spacing. Furthermore, XRD reveals that both samples consist out of three constituting parts. These are (a) pure MXene phase indicated by the aforementioned emerging (002) diffraction peak, (b) residual MAX phase that was not etched properly and (c) impurity phases like Li_3AlF_6 and LiF introduced during the etching process. (b) and (c) are electrochemically inactive and the exact mass contributions of these three constituting parts could not be determined. Both MXenes feature a typical accordion-like morphology resolved via SEM. GCPL measurements display a significant increase in specific capacity of 335 mA h g^{-1} in Mn- V_2C after 150 cycles at 0.1 A g^{-1} , which exceeds the specific capacity of 256 mA h g^{-1} in V_2C by more than 30% . This increase in specific capacity is also observed at high current densities up to 2000 cycles. Thereby, both samples demonstrate an excellent cycling stability as well as an almost perfect Coulomb efficiency of $> 99\%$. CV and GCPL measurements displayed at the first glance a novel oxidation process for Mn- V_2C . Intensive GCPL measurements however revealed, that after several cycles, also V_2C displays the same electrochemical behavior. As this phenomenon is present in both samples, a link to Mn can be ruled out. The origin of this process, which either arises from the MXene phase or an impurity, is unclear and needs further investigations. A possible explanation for the increased capacity in Mn- V_2C could be the increased interlayer spacing of Mn- V_2C compared to V_2C , which increases Li-ion transport properties and leads to faster kinetics. EIS thereby revealed a decreased charge transport resistance by $> 25\%$ in Mn- V_2C . Furthermore, different mass proportions of the constituting parts of the samples may lead to different specific capacities. For instance, V_2C could feature more electrochemically inactive residual precursor material and impurity phase compared to Mn- V_2C , resulting in a decreased specific capacity. Therefore, the increase in specific capacity of Mn- V_2C cannot unambiguously be assigned to the influence of Mn-doping. For that, two completely pure MXenes with no impurities or two MXenes featuring the exact same amount of same impurities needs to be prepared, wherein one sample is Mn-doped.

4 Comparison of the Effect of different Etching Solvents for MXene Synthesis

In the early stage of MXene development, the usage of HF acid was a common method to perform the A-phase exfoliation from the MAX precursor [6]. Due to the high harmfulness and toxicity of HF acid, the investigation in alternative etching methods increased drastically. As one of first alternatives, Ammoniumhydrogendifluorid (NH_4HF_2) can be used as a milder etchant with less health risk for the executor during the synthesis process, thereby also obtaining high purity MXenes [63]. Another option is the usage of fluorine salts with HCl, which was firstly suggested by [64]. Besides an overall safer synthesis process, this methods possesses the advantage that the fluorine salts exhibit metallic cations like Li^+ and Na^+ , which may be inserted into the interlayer sites of the MXenes [65]. This increases the interlayer spacing and prevents nanosheet self-stacking phenomena [66], which is beneficial for battery performance.

This chapter investigates the impact on the battery performance of different etching solvents used during the synthesis process of MXenes. Dr. Peng Guo synthesized two Mn-doped V_2C MXenes by each applying solutions of $\text{HCl} + \text{LiF}$ or $\text{HCl} + \text{NaF}$ on a Mn-doped V_2AlC MAX precursor. The resulting MXenes are labelled by $\text{Mn}-\text{V}_2\text{C}(\text{LiF})$ and $\text{Mn}-\text{V}_2\text{C}(\text{NaF})$ MXenes, according to which etching solution was applied. In the following, $\text{Mn}-\text{V}_2\text{C}(\text{NaF})$ is characterized structurally and electrochemically using XRD, SEM, EDS, XPS, CV, GCPL and EIS, while as a comparison characterization data of $\text{HCl} + \text{LiF}$ are also presented (this was already discussed in chapter 3).

4.1 Physical Characterization

To determine the crystallinity and the composition of the two powder samples, XRD measurements were performed. Fig. 4.1 shows the XRD pattern of the $\text{Mn}-\text{V}_2\text{C}(\text{LiF})$ and $\text{Mn}-\text{V}_2\text{C}(\text{NaF})$ MXenes synthesized with different etching solutions $\text{HCl} + \text{LiF}$ and $\text{HCl} + \text{NaF}$ (both in black). As a reference, the XRD pattern of the precursor material $\text{Mn}-\text{V}_2\text{AlC}$ (in blue) is plotted. Furthermore, reference pattern of Li_3AlF_6 and $\text{Na}_5\text{Al}_3\text{F}_{14}$ (in green and orange, respectively) are plotted. In order to address the origin of the visible peaks inside the diffractograms of the MXenes, their peaks were labeled with markers. The color used, symbolise the phase to which these peaks were attributed. Blue square labels are assigned to diffraction peaks of residual parental MAX phase $\text{Mn}-\text{V}_2\text{AlC}$, green and orange asterisk labels are assigned to diffraction peaks of Li_3AlF_6 and $\text{Na}_5\text{Al}_3\text{F}_{14}$, respectively. $\text{Mn}-\text{V}_2\text{C}(\text{NaF})$ features traces of residual MAX phase and $\text{Na}_5\text{Al}_3\text{F}_{14}$. Furthermore, it exhibit a new peak emerging at $2\theta < 10^\circ$, which is assigned to the (002)

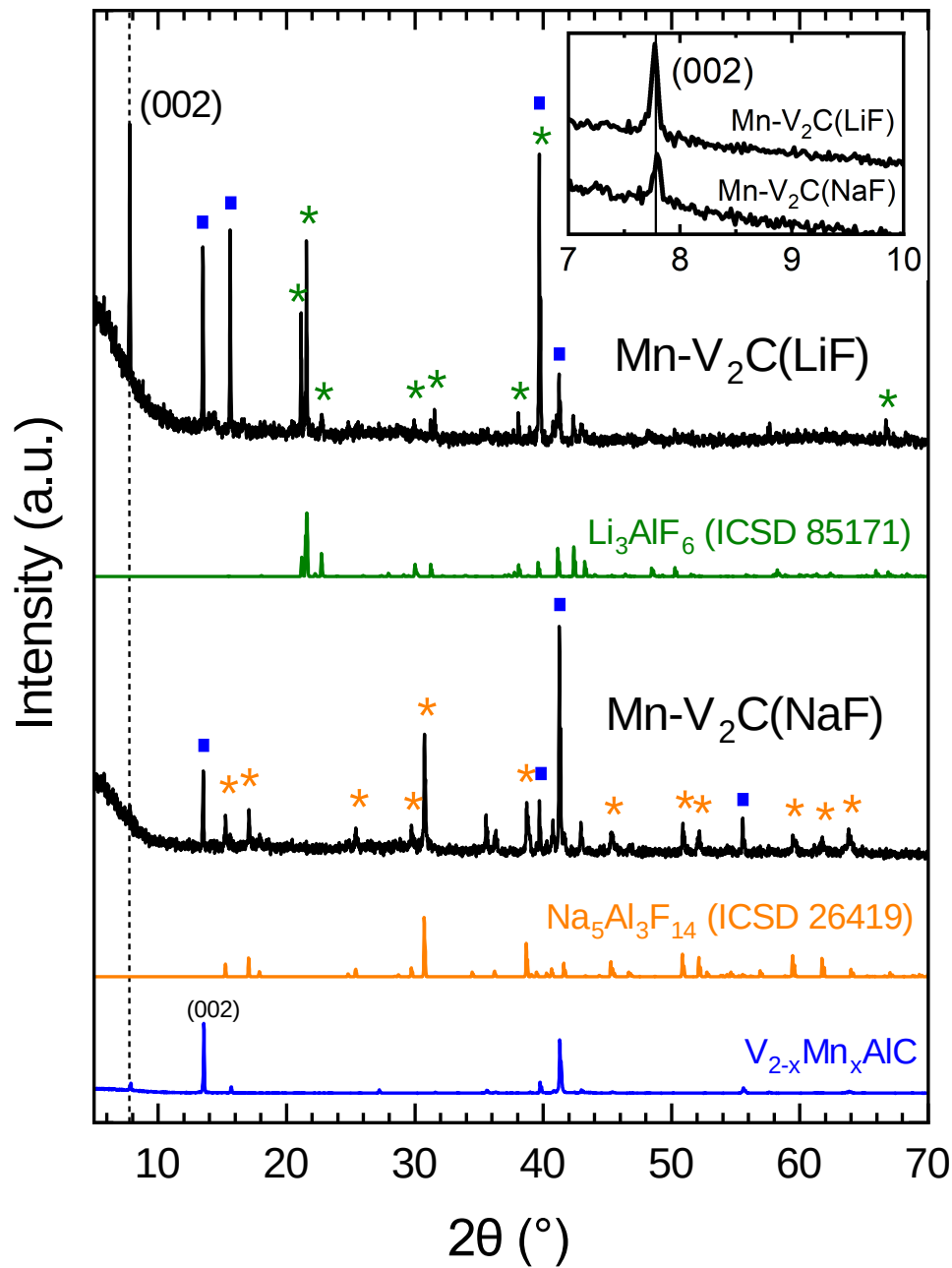
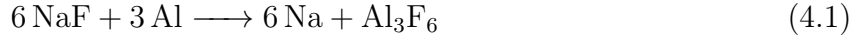


Figure 4.1: XRD patterns of Mn-V₂C(LiF) and Mn-V₂C(NaF) (both black), synthesized using solutions of HCl + LiF and HCl + NaF, respectively, together with reference pattern of the precursor material Mn-V₂AlC (blue), as well as impurity phases Li₃AlF₆ (green, [12] Coll. Code 85171) and (orange, [12] Coll. Code 26419). Labels on the Mn-V₂C(LiF) and Mn-V₂C(NaF) represented as blue squares are associated with the precursor material, green and orange asterisks are associated with Li₃AlF₆ and Na₅Al₃F₁₄ impurity phases introduced during the etching process. The (002) diffraction of Mn-V₂C(LiF) and Mn-V₂C(NaF) is highlighted with a dashed black line and enlarged in the inset.

diffraction peak of MXene phase. It is weakly pronounced and only observable in the inset. The XRD pattern clearly reveals that similar to $\text{Mn-V}_2\text{C}(\text{LiF})$, $\text{Mn-V}_2\text{C}(\text{NaF})$ consist out of a mixture of three constituting parts, i.e. pure MXene phase, residual MAX phase and $\text{Na}_5\text{Al}_3\text{F}_{14}$.

As already mentioned in chapter 3.1, the dominant diffraction peak related to pure MXene phase is the (002) diffraction observed in the XRD. It shifts to lower angles compared to the precursor material, which demonstrates the successful synthesis of MXene phase. $\text{Mn-V}_2\text{C}(\text{NaF})$ thereby features a significantly weaker reflex, suggesting that the etching process did not take place as accurately as in $\text{Mn-V}_2\text{C}(\text{LiF})$. It also indicates a higher amount of residual precursor material. The (002) diffraction peak of $\text{Mn-V}_2\text{C}(\text{LiF})$ and $\text{Mn-V}_2\text{C}(\text{NaF})$ are at the exact same angle θ , as highlighted in the inset of Fig. 4.1, which indicates equal interlayer spacings of $c = 6.74(1) \text{ \AA}$ (see chapter 3.1 table 3.1). Besides the new emerging (002) diffraction peak, the XRD pattern of $\text{Mn-V}_2\text{C}(\text{NaF})$ feature residual MAX phase, as well as a $\text{Na}_5\text{Al}_3\text{F}_{14}$ impurity introduced during the etching process, also observed in literature [11]. Similar to the chemical formation process of Li_3AlF_6 shown in the reaction equations 3.1, $\text{Na}_5\text{Al}_3\text{F}_{14}$ is assumed to be formed alike:



Here, the Al from the A phase of the precursor reacts with NaF of the etching solvent, resulting in Al_3F_6 . This reacts again with NaF to $\text{Na}_5\text{Al}_3\text{F}_{14}$.

In order to determine the elemental distribution as well as the oxidation states of the MXenes, XP spectra were recorded. Fig. 4.2(a) shows survey spectra from 0 to 700 eV of $\text{Mn-V}_2\text{C}(\text{LiF})$ and $\text{Mn-V}_2\text{C}(\text{NaF})$ in red and blue, respectively. Similar to $\text{Mn-V}_2\text{C}(\text{LiF})$, in $\text{Mn-V}_2\text{C}(\text{NaF})$ all mayor expected elements (V, C, F, Al and O) were identified. Furthermore, a weak signal of Mn is observable. $\text{Mn-V}_2\text{C}(\text{NaF})$ also features a signal associated to In as well as a signal at 269 eV, labelled with a black asterisk. Similar to $\text{Mn-V}_2\text{C}(\text{LiF})$, the mayor expected elements in $\text{Mn-V}_2\text{C}(\text{NaF})$ could indicate the existence of pure MXene phase, residual MAX phase and impurity phase. In addition to that, the In3d signal survey spectrum originates from the used In substrate, onto which the powder sample is fixed during sample preparation. The strong signal observed at 269 eV cannot be assigned to any element and is of unknown origin. Also, there is no Na1s signal observed in this spectrum because its binding energy is in the range of $> 1070 \text{ eV}$. All in all, the XP survey spectrum of $\text{Mn-V}_2\text{C}(\text{LiF})$ and $\text{Mn-V}_2\text{C}(\text{NaF})$ in Fig. 4.2(a) is in good consensus with XRD pattern in 4.1.

Fig. 4.2(b) shows the V2p state core level spectrum. $\text{Mn-V}_2\text{C}(\text{NaF})$ features two clean peaks at 524.2 eV and 517 eV, which correspond to V^{4+} [18]. However, V^{2+} could not be observed. Thus, V in $\text{Mn-V}_2\text{C}(\text{NaF})$ occurs only in one oxidation state. Fig. 4.2(c) shows the Mn2p state core level spectrum. The signal is too noisy to confirm the expected Mn^{4+} oxidation state. Similar to $\text{Mn-V}_2\text{C}(\text{LiF})$, the exact oxidation state of Mn in $\text{Mn-V}_2\text{C}(\text{NaF})$ cannot be extracted. Fig. 4.2(d) shows the C1s state core level spectrum. The C1s state spectrum of $\text{Mn-V}_2\text{C}(\text{NaF})$ features two light peaks at 284.6 eV

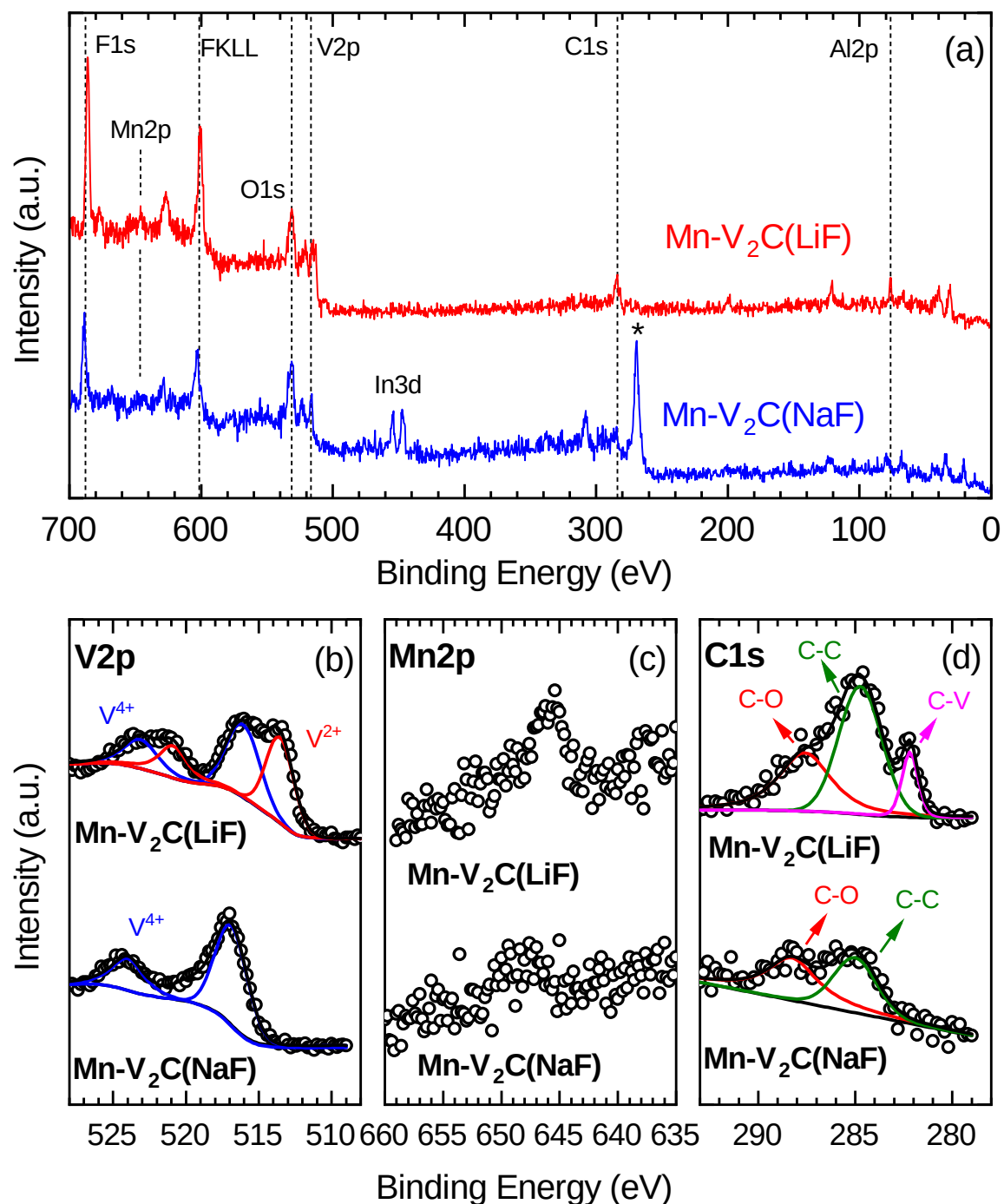


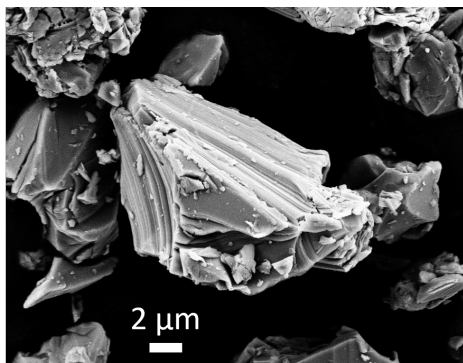
Figure 4.2: XPS spectra of Mn-V₂C(LiF) and Mn-V₂C(NaF). (a) shows survey spectra with vertical dashed lines as markers of the main constituting elements. (b-d) show core level spectra of V2p, Mn2p and C1s states, respectively. The lines display fits according to the presumed spectral contribution. XPS spectra were recorded and fitted by Prof. Dr. Michael Zharnikov at the Institute of Applied Physical Chemistry at Heidelberg University.

and 288.2 eV. These reveal the coexistence of the chemical bonds C—O (red) and C—C (green) [18].

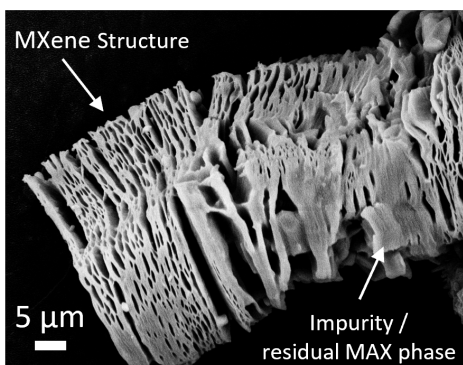
In order to investigate morphology differences, SEM measurements were performed. Fig. 4.3 shows SEM images of (a) Mn—V₂AlC before the synthesis as well as (b) Mn—V₂C(LiF) and (c) Mn—V₂C(NaF) after the synthesis. The precursor material in Fig. 4.3(a) displays densely packed particles in the range of several micrometers. Performing the synthesis process using HCl + LiF completely changes the morphology. The SEM image of Mn—V₂C(LiF) in Fig. 4.3(c) has a clean accordion-like shape. Most parts thereby have a very open lamella structure labelled as "MXene structure", while some minor parts look more dense, labelled as "impurity". In comparison, performing the synthesis process using HCl + NaF also fundamentally changes the morphology. But the SEM image of Mn—V₂C(NaF) in Fig. 4.3(c) features two completely different phases. The first phase, indicated in a darker contrast, exhibits a dense accordion-like structure with only little amount of void space, labelled as "MXene structure". The second phase indicated in a lighter contrast, exhibits random oriented short sticks laying on the surface of the first phase, labelled as "impurity".

In order to identify different phases observed in SEM, EDS measurements were performed, which results can be found right next to the SEM images in Fig. 4.3. The precursor Mn—V₂AlC features 32.8(10) % Al mass contribution. In contrast, Mn—V₂C(LiF) features 7.2(10) % of Al on the open MXene structure. The reduction in the amount of Al reveals the successful etching process, nevertheless acts like a measure for the amount of residual precursor material in the sample. 7.2(10) % of Al suggest that a high quantity of residual MAX phase was not etched properly. Parts labelled as "impurity" with a more dense morphology exhibit 35.5(30) % of Al, suggesting that these Al accumulations correspond to residual MAX phases. The identification of the MAX phase is in agreement with XRD pattern in Fig. 4.1. In contrast, Mn—V₂C(NaF) exhibits 18(3) % Al on the MXene structure (first observed phase with a darker contrast). Again, the reduction in the amount of Al compared to the precursor material reveals the successful etching process, however featuring a lot of residual MAX phase. In direct comparison to Mn—V₂C(LiF), Mn—V₂C(NaF) has approx. 2.5x more Al, which suggests a higher quantity of residual MAX phase. This explains, why the MXene morphology of Mn—V₂C(NaF) looks more dense with less void space compared to Mn—V₂C(LiF). The second phase indicated in a lighter contrast features 10.2(8) % of Na, 14.5(10) % of Al and 77.3(7) % of F. This is assigned to Na₅Al₃F₁₄, already observed in XRD in Fig. 4.1. All in all, the exact mass contributions of pure MXene phase, residual MAX phase and impurity phases in Mn—V₂C(LiF) and Mn—V₂C(NaF) could not be extracted. But quantitative analysis reveals that compared to Mn—V₂C(LiF), Mn—V₂C(NaF) features a less pronounced MXene structure with less void space, higher amount of residual MAX phase and obvious impurities on the surface of the sample.

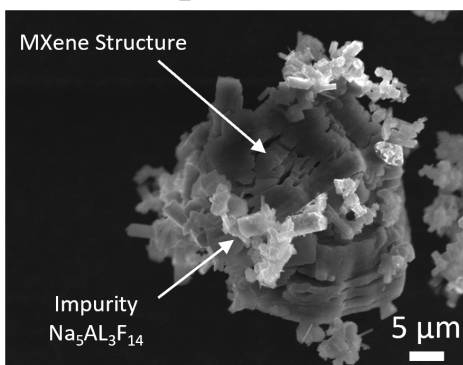
EDS analysis also gives information about mass contributions of other elements. But these results can not be considered impeccable, since many characteristic element transitions overlap each other in the EDS histogram such that it is impossible to differentiate between many elements. For example, EDS measures 79.6(15) % of V and 0 % of O, C and F in

(a) Mn-V₂AlC Precursor

on Particle:	Al: 32.8(10) %
	Mn: 2.8(5) %

(b) Mn-V₂C(LiF) MXene

on MXene Structure:	Al: 7.2 (10) %
	Mn: 0.76(42) %
on Impurity:	Al: 35.5(30) %

(c) Mn-V₂C(NaF) MXene

on MXene Structure:	Al: 18(3) %
on Impurity:	Na: 10.2(8) %
	Al: 14.5(10) %
	F: 77.3(7) %

Figure 4.3: SEM images of (a) precursor Mn-V₂AlC as well as corresponding (b) Mn-V₂C(LiF) and (c) Mn-V₂C(NaF) MXene, synthesized with etching solvents HCl + LiF and HCl + NaF, respectively. Right next to the SEM images are listed EDS results of certain constituting elements.

Mn-V₂C(LiF), because the V L α transition overlaps with O K α , C K α , Cl L α and F K α . This is in clear contradiction to XPS results in Fig.4.2 which show strong O, C and F photoelectron signals. However, safe to compare are the Al contributions because the Al K α transition does not overlap with any other transitions of constituting elements. To avoid this problem and to determine the amount of C, H and N, EA was also performed, which results are given in table 4.1, and are left to the interested reader.

Table 4.1: EA results of several samples, including the precursor Mn-V₂AlC, as well as the the MXenes Mn-V₂C(LiF) and Mn-V₂C(NaF).

Sample	Element	%
Mn-V ₂ AlC	C	8.72(2)
	H	0.13(20)
	N	0.36(10)
Mn-V ₂ C(LiF)	C	4.61(2)
	H	1.73(20)
	N	0
Mn-V ₂ C(NaF)	C	4.36(2)
	H	1.29(20)
	N	0.05(10)

4.2 Electrochemical Characterization

In order to evaluate the electrochemical performance of the two MXenes, GCPL measurements were performed and will be discussed in the following. While the XRD pattern in Fig. 4.1 reveals that Mn-V₂C(NaF) consists out of several constituting parts, i.e. pure MXene phase, residual MAX phase and Na₅Al₃F₁₄ impurity, the electrochemical activity of these additional phases will be considered first. Chapter 3.2 already showed that the MAX phase is electrochemically inactive. This also holds for Na₅Al₃F₁₄ [11], thus, it does not influence electrochemical processes in the material but contributes to the sample by weight.

Fig. 4.4 shows GCPL measurements of the two MXenes. Fig. 4.4(a) shows specific capacities of Mn-V₂C(LiF) (red) and Mn-V₂C(NaF) (blue) at a (dis-)charging current of 0.1 A g⁻¹ over the first 150 cycles with corresponding Coulomb efficiencies in light red and light blue, respectively. Mn-V₂C(NaF) exhibits an initial capacity of 415 mA h g⁻¹, which drops to 178 mA h g⁻¹ and saturates at 223 mA h g⁻¹. This course is very similar to the specific capacity of Mn-V₂C(LiF), just shifted to lower capacity values. Fig. 4.4 shows potential profiles of Mn-V₂C(LiF) (red) and Mn-V₂C(NaF) (blue) after 100 cycles at a (dis-)charging current of 0.1 A g⁻¹. As demonstrated in Fig. 4.4(a), Mn-V₂C(LiF) exhibits a higher specific capacity, which is also visible here. The potential profiles of both samples feature a similar linear behavior. During charge, light oxidation bumps are

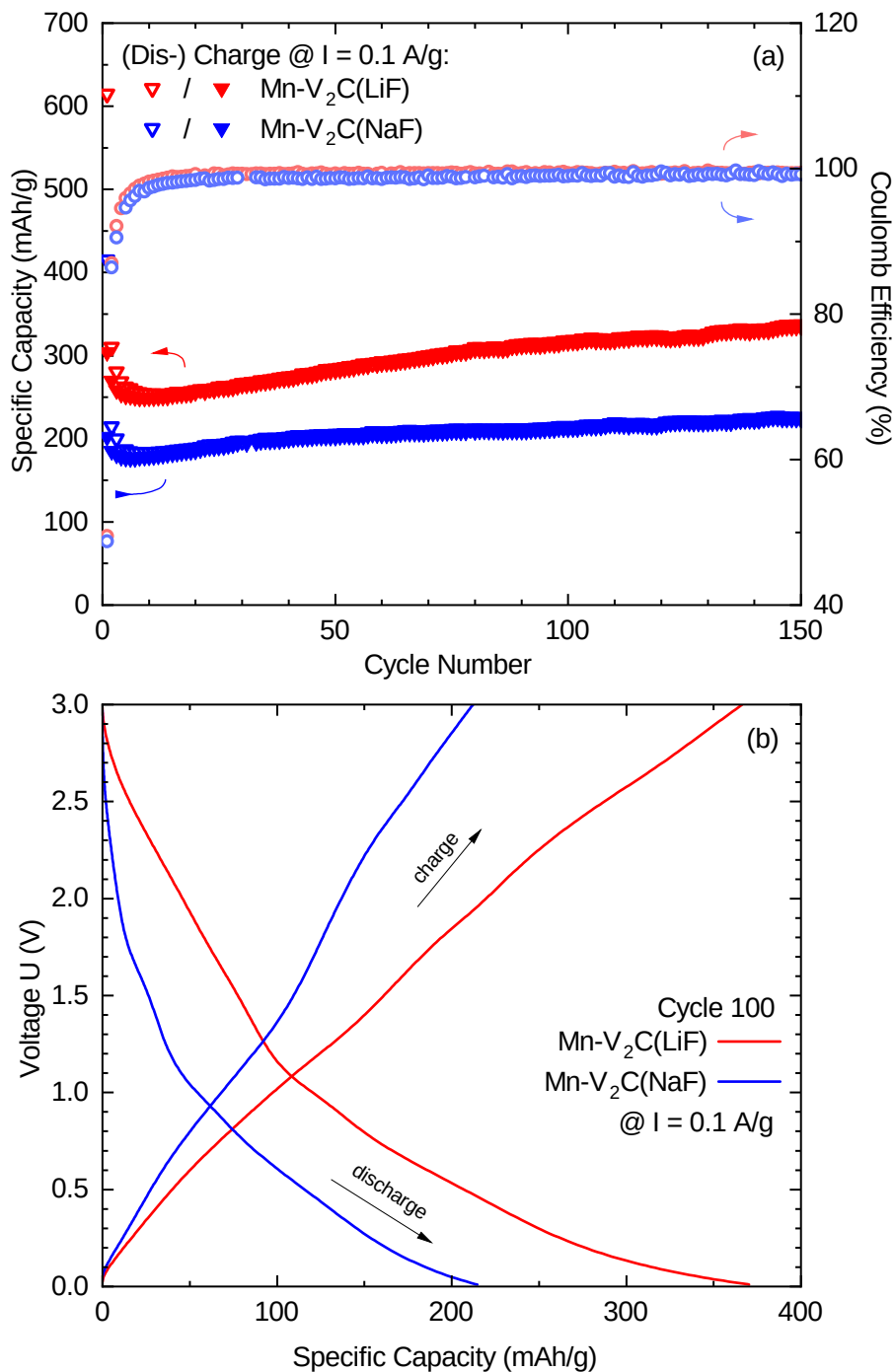


Figure 4.4: (a) Specific discharge and charge capacities of Mn- $\text{V}_2\text{C}(\text{LiF})$ (red) and Mn- $\text{V}_2\text{C}(\text{NaF})$ (blue) electrodes at 100 mA g^{-1} obtained in the voltage regime from 0.01 to 3 V. (b) GCPL potential profiles of cycle 100 of Mn- $\text{V}_2\text{C}(\text{LiF})$ (red) and Mn- $\text{V}_2\text{C}(\text{NaF})$ (blue) at 0.1 A g^{-1} .

observable at approx. 1.3 V and 1.9 V, wherein during discharge, light reduction bumps are observable at 1.1 V and 0.7 V. Fig. 4.4 clearly reveals an increase in specific capacity of almost 50 % for Mn–V₂C(LiF) over Mn–V₂C(NaF), thereby featuring similar potential profiles. In the following, these results will be discussed in detail.

The loss in specific capacity of Mn–V₂C(NaF) after the first cycle is attributed to irreversible processes, in particular to SEI formation [30, 31]. Subsequent increase in specific capacity is related to the material becoming more amorphous upon cycling. After 150 cycles, Mn–V₂C(LiF) has an increased specific capacity of almost 50 % over Mn–V₂C(NaF), thereby featuring an almost perfect Coulomb efficiency of > 99 %. In order to evaluate the origin of the difference in specific capacity, Fig. 4.4(b) plots the potential profiles of Mn–V₂C(LiF) and Mn–V₂C(NaF) at cycle 100. As described above, their potential profiles look very similar and feature bumps in alike voltage regions. This suggests that only the same and no new processes are taking place in the samples. That is reasonable since both samples should have the exact same electrochemical properties after a theoretically ideal synthesis process, in which the whole Al phase was perfectly exfoliated. Since the synthesis processes performed in this work lead to several impurities as discussed in chapter 4.1, the difference in specific capacity rather originates from somewhere else. For example, different mass contributions of the constituting parts of the samples may lead to different specific capacities. Mn–V₂C(LiF) features minor residual MAX phase and a relatively clean accordion-like morphology with a lot of void space, extracted from XRD (see Fig. 4.1) and SEM (see Fig. 4.3(b)). In contrast, Mn–V₂C(NaF) has a higher amount of residual MAX phase, also proposed by XRD (see Fig. 4.1) and confirmed by EDS (see Fig. 4.3). Furthermore, SEM and EDS results reveal the existence of a lot of clearly visible Na₅Al₃F₁₄ impurity on the surface of Mn–V₂C(NaF). A higher amount of residual, electrochemically inactive MAX phase and electrochemically inactive Na₅Al₃F₁₄ contributes in weight that decreases the specific capacity. Furthermore, the accordion-like structure of Mn–V₂C(NaF) (see Fig. 4.3(c)) looks more dense with less void space compared to Mn–V₂C(LiF). This may offer less space for the electrolyte to penetrate the material, leading to potentially decreased Li-ion transport properties.

In order to evaluate the kinetics and the supposed differences in charge transport properties of the MXenes, EIS measurements were performed. Fig. 4.5 shows a Nyquist plot of Mn–V₂C(LiF) (red) and Mn–V₂C(NaF) (blue) after OCV. Similar to Mn–V₂C(LiF), Mn–V₂C(NaF) features a slight offset on the x-axis in the high frequency range corresponding to the bulk resistance, a half-circle behavior in the high to medium frequency range corresponding to charge transport properties and a linear increase in the low frequency range related to diffusion processes. The equivalent circuit shown in the inset of Fig. 4.5 used to fit the half-circle consists out of a resistance R_1 connected in series with a resistance R_2 and a capacitance C_2 that are connected in parallel. Their values are given in table 4.2.

The bulk resistance R_1 of Mn–V₂C(LiF) and Mn–V₂C(NaF) are almost identical. However, the half circle radius has significantly changed, indicating different charge transport resistances. While Mn–V₂C(LiF) features a charge transport resistance R_2 of 52.7(3) Ω , Mn–V₂C(NaF) features a strongly increased value of 452(20) Ω . This adds up to the

aforementioned results and confirms the above expectation that a higher amount of residual MAX phase, a more closed and dense MXene structure and a lot of impurity phase deposited on the surface of Mn–V₂C(NaF) lead to suppressed charge transport properties and a significantly decreased battery performance.

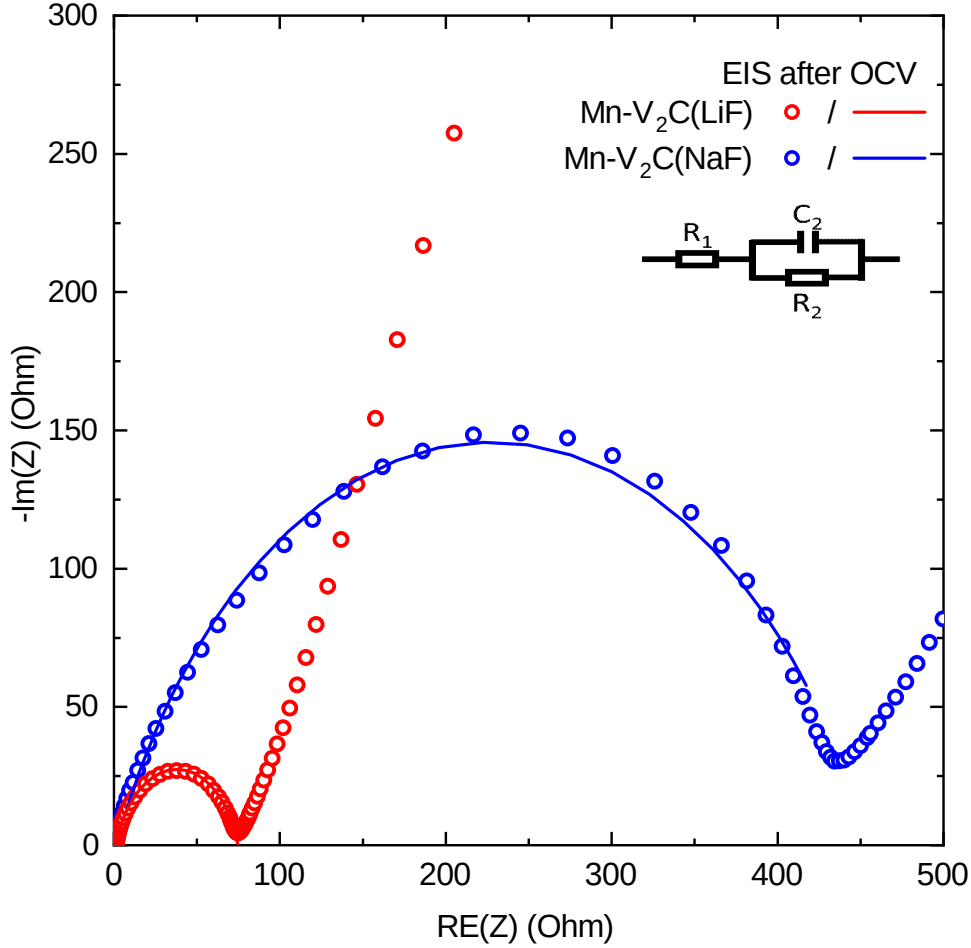


Figure 4.5: Nyquist plot of impedance measurements on Mn–V₂C(LiF) (red) and Mn–V₂C(NaF) (blue) after OCV. Solid lines represent fits of the equivalent circuit shown in the inset.

Table 4.2: Extracted values of the EIS equivalent circuit elements R_1 , R_2 and C_2 used for the EIS fit of Mn–V₂C(LiF) and Mn–V₂C(NaF). The error values were extracted by altering the fitting parameters to an insufficient fit.

Sample	$R_1(\Omega)$	$R_2(\Omega)$	$C_2(\mu F)$
Mn–V ₂ C(LiF)	1.3(1)	52.7(3)	3.7(2)
Mn–V ₂ C(NaF)	1.4(1)	452(20)	1.8(2)

4.3 Conclusion for Comparison of Etching Solvents

In this work, the impact of the usage of different etching solvents during the synthesis process of Mn–V₂C MXenes was investigated. Thereby, the samples Mn–V₂C(LiF) and Mn–V₂C(NaF) were etched by exfoliating the Al phase of a Mn–V₂AlC precursor using a solution of HCl + LiF or HCl + NaF, respectively. Both MXenes exhibit an emerging (002) diffraction peak at $2\theta < 10^\circ$ in XRD measurements, which demonstrates an increased interlayer distance compared to the precursor material and confirms the successful synthesis of pure MXene phase. While this peak is strongly pronounced in the XRD pattern of Mn–V₂C(LiF), it is only very weak and almost invisible in the XRD pattern of Mn–V₂C(NaF), suggesting that Mn–V₂C(NaF) comprises more residual MAX phase. This was further confirmed by measuring the amount of Al via EDS, wherein Mn–V₂C(NaF) exhibits 2.5x more Al compared to Mn–V₂C(LiF). XRD also reveals that both samples consist out of three main constituting parts. These are (a) pure MXene phase indicated by the aforementioned emerging (002) diffraction peak, (b) residual MAX phase that was not etched properly and (c) impurity phases Li₃AlF₆/Na₅Al₃F₁₄ introduced during the etching process. (b) and (c) are electrochemically inactive and the exact mass contributions of these three constituting parts could not be determined. SEM images display a typical accordion-like morphology for both samples. While Mn–V₂C(LiF) features an wide open lamella structure, the structure of Mn–V₂C(NaF) looks more dense and closed with a high amount of Na₅Al₃F₁₄ on the sample surface. GCPL measurements display a significantly higher specific capacity in Mn–V₂C(LiF) by almost 50 %. Several explanations for this drastic difference are brought forth. EDS reveals that Mn–V₂C(NaF) features a higher amount of residual and electrochemically inactive MAX phase, which decreases specific capacity. Also, a more closed MXene structure and a large amount of impurity phase on the surface of the sample may hinder easy electrolyte penetration, reducing Li-ion transport properties. EIS also revealed a strongly increased charge transport resistance in Mn–V₂C(NaF). All in all, this work shows an increased battery performance of Mn–V₂C when using HCl + LiF, compared to HCl + NaF as an etching solvent during the synthesis process. It thus suggests HCl + LiF over HCl + NaF as an etching solvent for Mn–V₂C MXene synthesis.

5 Investigations on $\text{Mo}_{4/3}\text{B}_2$ MBenes

The $\text{Mo}_{4/3}\text{B}_2$ MBene investigated in this work is synthesized by Dr. Peng Guo via the parental precursor material $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$ to $\text{Mo}_{4/3}\text{B}_2$ using a solution of $\text{HCl}+\text{LiF}$ as an etching solvent. As shown in Fig. 5.1, each layer also consists out of three sublayers Mo-B-Mo, exhibiting internal covalent bonding. Due to the periodic ordering of Y and Mo in the MAB phase and the subsequent removal of Y and Al, the Mo-sublattice in the MBene sample exhibits in-plane vacancy ordering. Besides excellent cycling stability and conductivity [67], $\text{Mo}_{4/3}\text{B}_2$ promises a high theoretical capacity of $C_{\text{theo},\text{Mo}_{4/3}\text{B}_2} = 358 \text{ mA h g}^{-1}$ using eq. 2.7, considering two electrons inserted in each structural unit. This work characterizes $\text{Mo}_{4/3}\text{B}_2$ structurally and electrochemically using XRD, SEM, XPS, CV and GCPL when used as an anode material for LIB.

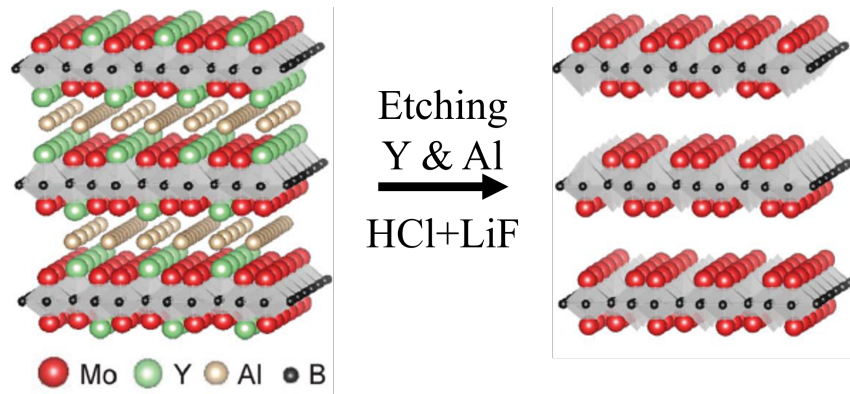


Figure 5.1: Crystallographic structures of parental $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$ MAB phase (left) and $\text{Mo}_{4/3}\text{B}_2$ MBene (right). Mo, Y, Al and B atoms are represented in red, green, beige and black, respectively. Extracted and adapted from [41].

5.1 Physical Characterization

In order to determine the chemical composition and the crystallographic structure of $\text{Mo}_{4/3}\text{B}_2$, XRD measurements were performed. Fig. 5.2 shows the XRD pattern of $\text{Mo}_{4/3}\text{B}_2$ (black), together with reference pattern of the precursor material $(\text{Mo}_{2/3}\text{Y}_{1/3})\text{AlB}_2$ (red). Furthermore, reference pattern of MoB , AlF_3 and Li_3AlF_6 are presented in blue, grey and green, respectively. In order to address the origin of the visible peaks inside the XRD pattern of $\text{Mo}_{4/3}\text{B}_2$, its peaks were labelled with markers. The color used, symbolise the phase to which these peaks were attributed. Firstly, red square labels are assigned to diffraction peaks of residual parental MAX phase $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$. Secondly, blue, grey

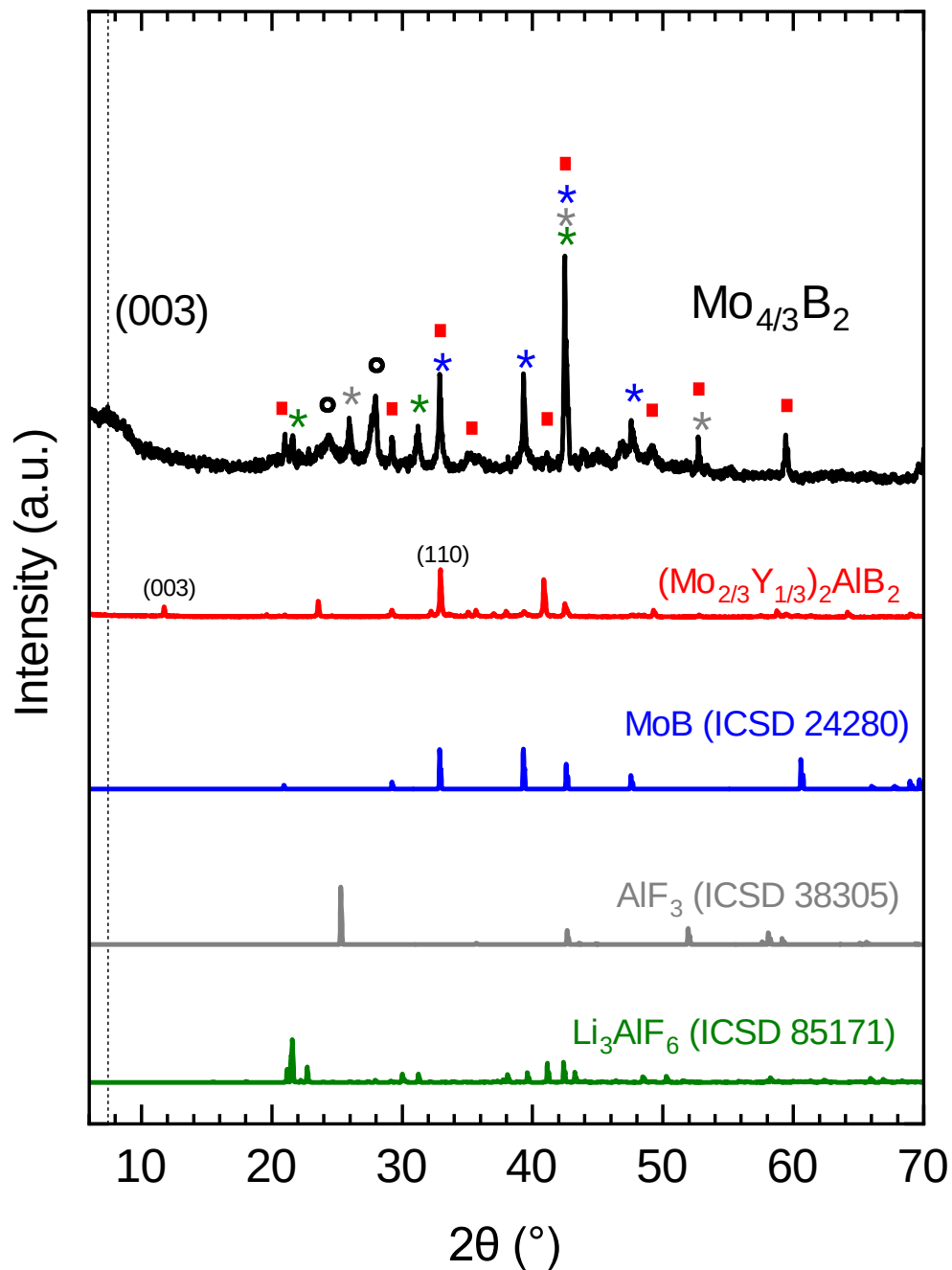


Figure 5.2: XRD patterns of $\text{Mo}_{4/3}\text{B}_2$ (black) together with reference pattern of the precursor material $(\text{Mo}_{2/3}\text{Y}_{1/3})\text{AlB}_2$ (red) and impurity phases MoB (blue, [12] Coll. Code 24280), AlF_3 (grey, [12] Coll. Code 38305) and Li_3AlF_6 (green, [12] Coll. Code 85171). Peaks with labels on the $\text{Mo}_{4/3}\text{B}_2$ pattern as red squares are associated with the precursor material, blue, grey and green asterisks are related to impurity phases MoB, AlF_3 and Li_3AlF_6 introduced during the etching process. Peaks labelled with a black circle cannot be assigned to a specific phase. The (003) diffraction of $\text{Mo}_{4/3}\text{B}_2$ is highlighted with dashed black lines.

and green asterisks labels are assigned to diffraction peaks of MoB, AlF_3 and Li_3AlF_6 , respectively. $\text{Mo}_{4/3}\text{B}_2$ features traces of residual MAB phase, as well as MoB, AlF_3 and Li_3AlF_6 . At $2\theta < 10^\circ$, a broad and low-intensity peak is occurring (indicated with a black dashed line), where the (003) diffraction of $\text{Mo}_{4/3}\text{B}_2$ is expected. Peaks labeled with a black circle cannot be assigned to any phase. The XRD pattern clearly reveals that $\text{Mo}_{4/3}\text{B}_2$ consists out of a mixture of several constituting parts, i.e. pure MBene phase, MoB, AlF_3 and Li_3AlF_6 .

The dominant diffraction peak related to pure $\text{Mo}_{4/3}\text{B}_2$ MBene phase is the (003) diffraction peak occurring in the low angle range [41]. The XRD pattern of $\text{Mo}_{4/3}\text{B}_2$ synthesized in this work only shows a broad peak of low intensity at $2\theta = 7.39^\circ$, which gives only a hint for the occurrence of the expected (003) diffraction peak. It cannot be clearly determined whether this broad peak really corresponds to the (003) diffraction peak, thus the clear existence of the expected pure MBene phase is unclear and the sample shows poor crystallinity. The XRD pattern of $\text{Mo}_{4/3}\text{B}_2$ also indicates a high amount of residual MAB phase that was not etched properly during the synthesis process. Furthermore, it features traces of MoB, AlF_3 and Li_3AlF_6 . These are impurity phases which were introduced during the etching process and were also observed in literature on $\text{Mo}_{4/3}\text{B}_2$ [41]. As already discussed in chapter 3.1, AlF_3 and Li_3AlF_6 are end products from the reaction of Al with LiF see eq. 3.1. In contrast, MoB is a new phase formed during the etching process. However, some peaks are labeled with a black circle, indicating that they could not be assigned to any phase. This suggests that not all impurities of the sample were determined. Since there is only one light peak associated to pure MBene phase and some peaks may originate from more than one impurity phase, the exact weight contribution of the above mentioned identified phases could not be extracted. All in all, XRD clearly reveals that $\text{Mo}_{4/3}\text{B}_2$ MBene synthesized in this work consists out of several constituting phases, i.e. residual MAB phase and impurity phases like MoB, AlF_3 and Li_3AlF_6 introduced during the etching process. The existence of pure $\text{Mo}_{4/3}\text{B}_2$ phase cannot be determined.

In order to determine the elemental distribution as well as the oxidation states of $\text{Mo}_{4/3}\text{B}_2$, XP spectra were recorded. Fig. 5.3(a) shows survey spectra of $\text{Mo}_{4/3}\text{B}_2$ from 0 to 700 eV. All major expected elements (Mo, B, F and O) were identified. Furthermore, a Y signal was detected. Mo3d and B1s state signals could indicate the existence of pure MBene phase or MoB impurity phase. Y3d and Al2p state signals likely show the existence of residual MAB phase. Strong F1s state and F_{KLL} Auger peak signals show the existence of F that was introduced during the etching process. Combined with the occurrence of Al, this also suggests the existence of AlF_3 and Li_3AlF_6 impurities, which were also identified in the XRD pattern. As already discussed in chapter 3.1 Li could not be detected due to its low characteristic sensitivity factor [56] and O1s state signals are detected because the sample was exposed to normal atmosphere. All in all, the XP survey spectrum of $\text{Mo}_{4/3}\text{B}_2$ in Fig. 5.3(a) is in good consensus with XRD pattern in 5.2.

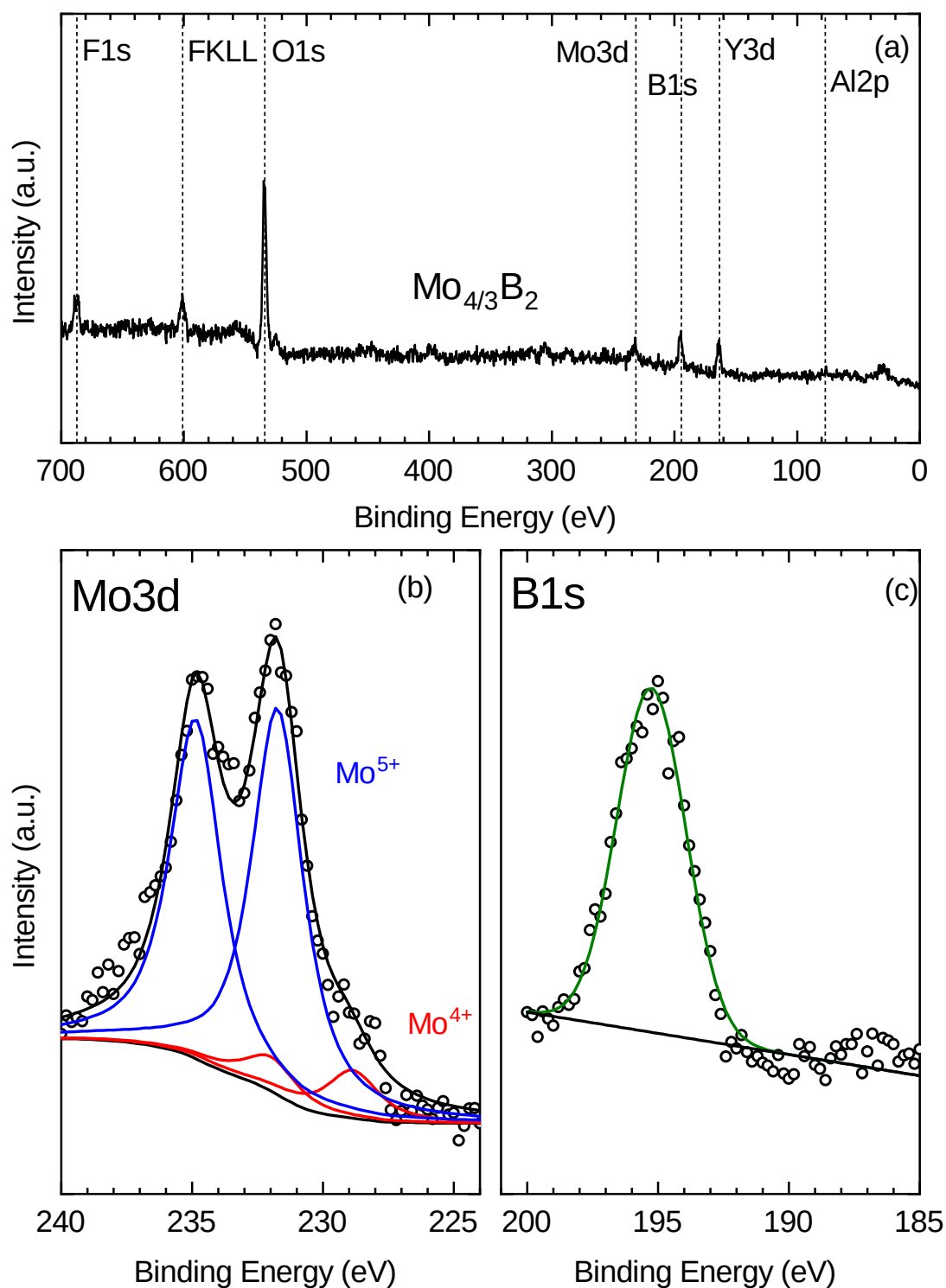


Figure 5.3: XP spectra of $\text{Mo}_{4/3}\text{B}_2$. (a) shows survey spectra with vertical dashed lines as markers of the main constituting elements. (b-c) show core level spectra of Mo3d and B1s states, respectively. The lines display fits according to the presumed spectral contribution. XP spectra were recorded and fitted by Prof. Dr. Michael Zharnikov at the Institute of Applied Physical Chemistry at Heidelberg University.

Fig. 5.3(b) shows the Mo3d state core level spectrum. $\text{Mo}_{4/3}\text{B}_2$ features two broad main peaks at 231.8 eV and 234.8 eV, wherein the first peak has a small right shoulder at 228.2 eV. The two main peak correspond to the Mo^{5+} oxidation state (fitted in blue) [18]. Furthermore, the right shoulder of the first peak suggests the existence of another low-intensity doublet state overlapping the two main peaks, corresponding to Mo^{4+} (fitted in red) [18]. Thus, Mo in $\text{Mo}_{4/3}\text{B}_2$ occurs in two oxidation states, i.e. Mo^{5+} and Mo^{4+} . The differences in the intensity signal Mo^{5+} suggests a much higher abundance of Mo^{5+} compared to Mo^{4+} .

Fig. 5.3(c) shows the B1s state core level spectrum. $\text{Mo}_{4/3}\text{B}_2$ features a strong peak at 195 eV (fitted in green). Reference literature [18] expects B1s state signals at ~ 5 eV lower binding energies. The observed B1s state signal is strongly shifted to higher energies, therefore no oxidation state can be extracted. B has an extremely low characteristic sensitivity factor [56], therefore it is also possible that the peak observed in Fig. 5.3(c) is from a different elemental state that is in the similar energy region as B1s. But no other elemental transition fits to this observed single peak, which leads to the determination that the origin of this peak is unknown.

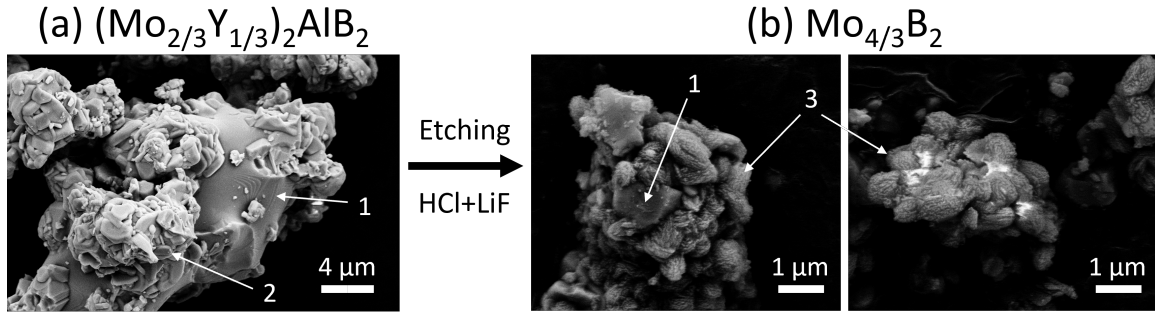


Figure 5.4: SEM images of (a) $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$ precursor material and (b) $\text{Mo}_{4/3}\text{B}_2$ MBene after the synthesis process.

To investigate the morphology of $\text{Mo}_{4/3}\text{B}_2$, SEM measurements were performed. Fig. 5.4 shows SEM images of (a) $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$ before the synthesis and (b) $\text{Mo}_{4/3}\text{B}_2$ after the synthesis. The SEM image of the precursor material in Fig. 5.4(a) displays densely packed clusters in the range of several micrometers with two different phases. The first phase (labelled as "1") consists out of big bulk particles featuring a clean and even surface. The second phase (labelled as "2") consists out of several smaller particles in an irregular pattern with random orientation. Performing the etching process leads to a partly change in morphology. The SEM image of $\text{Mo}_{4/3}\text{B}_2$ in Fig. 5.4(b) displays again clusters in the range of several micrometers with two different phases. The first phase (labelled as "1") has a clean and even surface and looks very similar to the first phase which was already observed in the precursor material in Fig. 5.4(a). The other, new phase (labelled as "3") shows oval-shaped particles with a coarse surface in the range of 1 μm .

The SEM images in Fig. 5.4 reveal that the applied synthesis leads to a partly changed morphology. While the SEM image of $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$ in Fig. 5.4(a) shows two different morphology phases, the SEM images of $\text{Mo}_{4/3}\text{B}_2$ in Fig. 5.4(b) also feature two different phases. The first observed phase in $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$ (labelled as "1") with a clean and even surface is also observed in $\text{Mo}_{4/3}\text{B}_2$ and is thus considered as (residual) MAB precursor material. The second phase (labelled as "2") does not appear in $\text{Mo}_{4/3}\text{B}_2$ anymore and indicates that it was etched during the synthesis process. The new phase (labelled as "3") with oval-shaped particles and a coarse surface does not appear in $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$ and is thus an end product of the synthesis process. Since these particles are sitting on the surface of the first phase, it seems as if the particles are formed from the MAB cluster. As discussed in chapter 2.5, the synthesis process of $\text{Mo}_{4/3}\text{B}_2$ MBene includes the exfoliation of Al and Y layers from the $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$ precursor. Due to the distinctive similarities of the synthesis processes between MBenes and MXenes, the expected morphology of $\text{Mo}_{4/3}\text{B}_2$ is also an accordion-like structure, for which the material class of MXenes is known [52, 53, 68]. Although there exist only few SEM images of MBenes, this typical lamella structure was already demonstrated for these boron based transition metal compounds [69, 70]. The fact that the $\text{Mo}_{4/3}\text{B}_2$ MBene investigated in this work does not feature the expected accordion-like morphology indicates an insufficient or even unsuccessful synthesis. All in all, the SEM images of $\text{Mo}_{4/3}\text{B}_2$ display the existence of residual MAB phase in the sample and could not exhibit typically expected MBene/MXene morphology. These results match with XRD results in Fig. 5.2, in which traces of residual MAB phase was also observed and pure $\text{Mo}_{4/3}\text{B}_2$ MBene phase could not be determined.

5.2 Electrochemical Characterization

In order to investigate the electrochemical activity of $\text{Mo}_{4/3}\text{B}_2$, CV and GCPL measurements were performed and will be discussed in the following. As discussed in chapter 5.1, the sample investigated in this work consists out of several constituting parts, i.e. residual MAB phase and impurity phases MoB, AlF_3 and Li_3AlF_6 . Thus, the electrochemical activities of these constituting parts will be considered first.

As already discussed in chapter 3.1, Li_3AlF_6 is electrochemically inactive. However, AlF_3 is used as a coating material for electrodes in LIB in order to increase battery performance [71–73]. Thus, it might be possible, that this impurity has an effect on electrochemical processes in the sample. MoB is a MBene by itself and can be synthesized by exfoliating the Al phase from a MoAlB precursor [69]. MoB is electrochemically active [69] and needs to be considered when analyzing CV and GCPL measurements of $\text{Mo}_{4/3}\text{B}_2$ MBene in this work. In order to investigate the electrochemical behavior of the precursor material, CV and GCPL measurements of $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$ are plotted in Fig. 5.5 and will be discussed in the following.

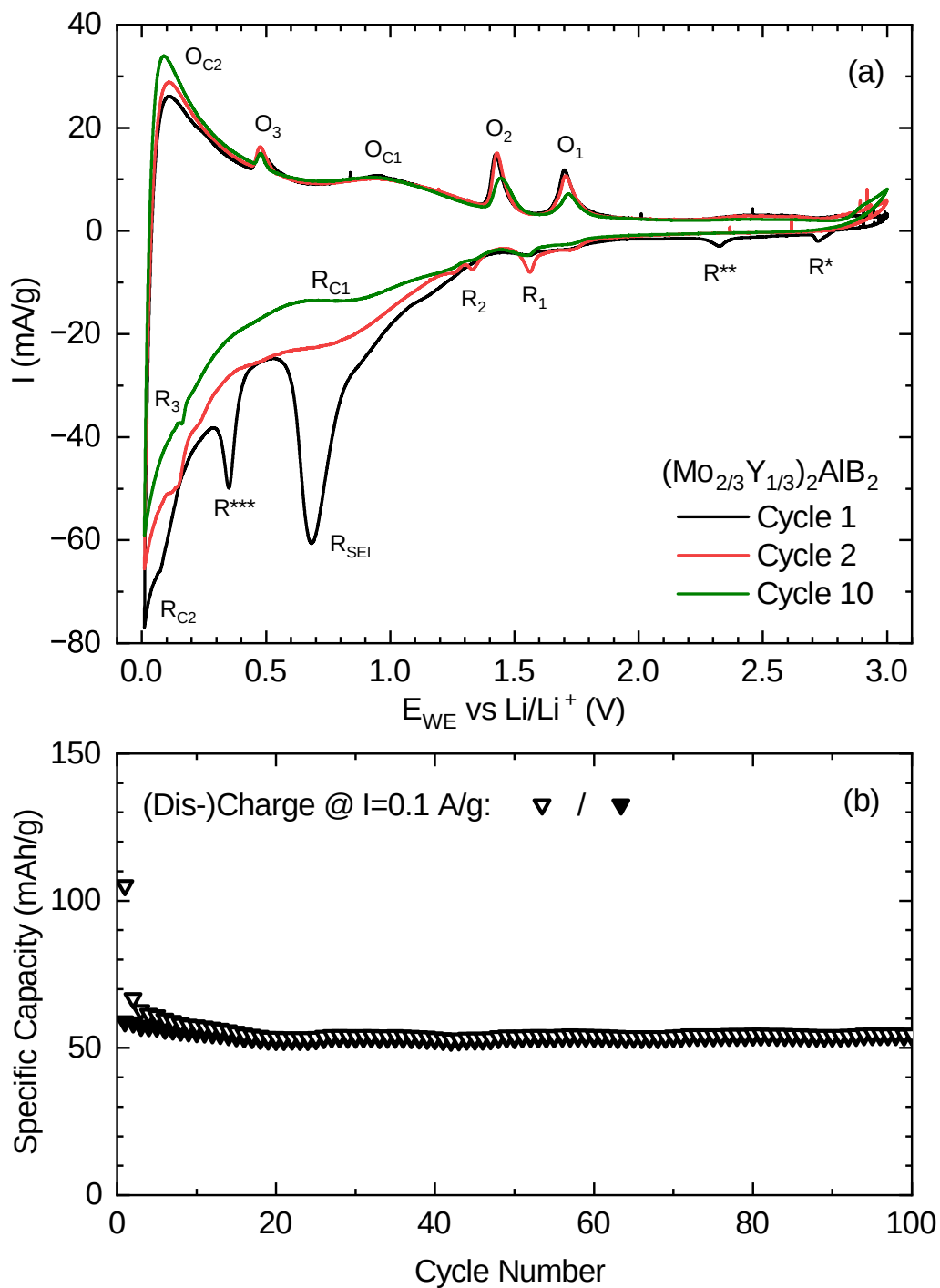


Figure 5.5: CV and GCPL measurements of $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$. (a) shows a CV of cycle 1, 2 and 10 (in black, red and green, respectively) measured at a scan rate of 0.1 mV s^{-1} . The labels R/O represent distinct reduction and oxidation peaks. (b) shows specific discharge and charge capacities at 0.1 A g^{-1} obtained in the voltage regime from 0.01 to 3 V.

Fig. 5.5(a) shows a cyclic voltammogram of $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$ at a scan rate of 0.1 mV s^{-1} . During the first discharge scan (indicated in black), several reduction peaks are observable at $R^* = 2.72 \text{ V}$, $R^{**} = 2.32 \text{ V}$, $R_1 = 1.56 \text{ V}$, $R_2 = 1.33 \text{ V}$, $R_{\text{SEI}} = 0.69 \text{ V}$, $R^{***} = 0.35 \text{ V}$, $R_3 = 0.08 \text{ V}$ and $R_{\text{C}2} = 0.01 \text{ V}$. During the first charge scan, several oxidation peaks are observable at $\text{O}_{\text{C}2} = 0.09 \text{ V}$, $\text{O}_3 = 0.48 \text{ V}$, $\text{O}_{\text{C}1} = 0.96 \text{ V}$, $\text{O}_2 = 1.43 \text{ V}$ and $\text{O}_1 = 1.70 \text{ V}$. In the second and 10th discharge scan (indicated in red and green, respectively) only the reduction peaks R_1 , R_2 , R_3 and $R_{\text{C}2}$, as well as a new peak at $R_{\text{C}1} = 0.78 \text{ V}$ are present. The second and 10th charge scan feature the same peaks which were already observed in the first charge scan. The CV of $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$ reveals several reduction and oxidation peaks which will be discussed in the following. The vanishing of the peaks R^* , R^{**} , R^{***} and R_{SEI} after the first cycle indicates irreversible behavior and are attributed to irreversible processes in the material. R_{SEI} is unambiguously assigned to SEI formation [30, 31]. All other reduction and oxidation peaks are reversible and are identified as redox pairs. Thereby, the most pronounced pairings are $R_{\text{C}1}/\text{O}_{\text{C}1}$ and $R_{\text{C}2}/\text{O}_{\text{C}2}$, which are assigned to the intercalation of Li-ions into electrochemically active CB, which is a constituent of the electrode, (compare with chapter 2.4 Fig. 2.5). The other three pairings R_1/O_1 , R_2/O_2 and R_3/O_3 are extremely weakly pronounced and convert only small currents. Fig. 5.5(a) clearly reveals that the CV of the $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$ precursor is dominated by CB contributions. Nevertheless, there are weak induced currents that can be assigned to redox processes taking place in $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$.

In order to evaluate the contribution of the $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$ precursor in specific capacity, GCPL measurements were performed. Fig. 5.5(b) shows specific capacities of $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$ at a (dis-)charging current of 0.1 A g^{-1} over the first 100 cycles. The initial specific capacity of 105 mA h g^{-1} drops after the first cycle and saturates quickly to 54 mA h g^{-1} . 20 % of weight proportion of CB in the working electrode contributes 45 mA h g^{-1} to the specific capacity. Thus, at a current of 0.1 A g^{-1} , a specific capacity of $\sim 10 \text{ mA h g}^{-1}$ is assigned as contribution from the $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$ precursor.

Taking into account the electrochemical activity of $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$, MoB and AlF_3 , the electrochemical activity of $\text{Mo}_{4/3}\text{B}_2$ is now investigated. Fig. 5.6 shows cyclic voltammograms of $\text{Mo}_{4/3}\text{B}_2$ measured at a scan rate of 0.1 mV s^{-1} . During the first discharge scan (indicated in black), several reduction peaks are observable at $R_1 = 1.47 \text{ V}$, $R_{\text{SEI}} = 0.67 \text{ V}$ and $R_{\text{C}2} = 0.01 \text{ V}$. During the first charge scan, several oxidation peaks are observable at $\text{O}_{\text{C}2} = 0.16 \text{ V}$, $\text{O}_3 = 0.71 \text{ V}$, $\text{O}_{\text{C}1} = 0.86 \text{ V}$, $\text{O}_2 = 1.41 \text{ V}$ and $\text{O}_1 = 1.70 \text{ V}$. In the 5th and 10th discharge scans (indicated in red and green, respectively) only the reduction peaks R_1 , R_2 and $R_{\text{C}2}$, as well as a new peak at $R_2 = 1.15 \text{ V}$ and $R_3 = 0.13 \text{ V}$ are present. The 5th and 10th charge scans feature the same oxidation peaks which were already observed in the first charge scan, with a slightly decreased intensity. Altogether, the CV reveals several reduction and oxidation peaks which will be discussed in the following.

In the CV of $\text{Mo}_{4/3}\text{B}_2$ in Fig. 5.6, the vanishing of the peak R_{SEI} is assigned to the irreversible formation of SEI [30]. The other reduction and oxidation peaks are assigned as redox pairs, i.e. R_1/O_1 , R_2/O_2 , R_3/O_3 and $R_{\text{C}2}/\text{O}_{\text{C}2}$. The CV signal between R_2 and R_3 does not decrease significantly, which indicates another reduction peak at $R_{\text{C}1} = 0.75 \text{ V}$ underlying beneath. This completes the last redox pair $R_{\text{C}1}/\text{O}_{\text{C}1}$. Analogous to the CV of

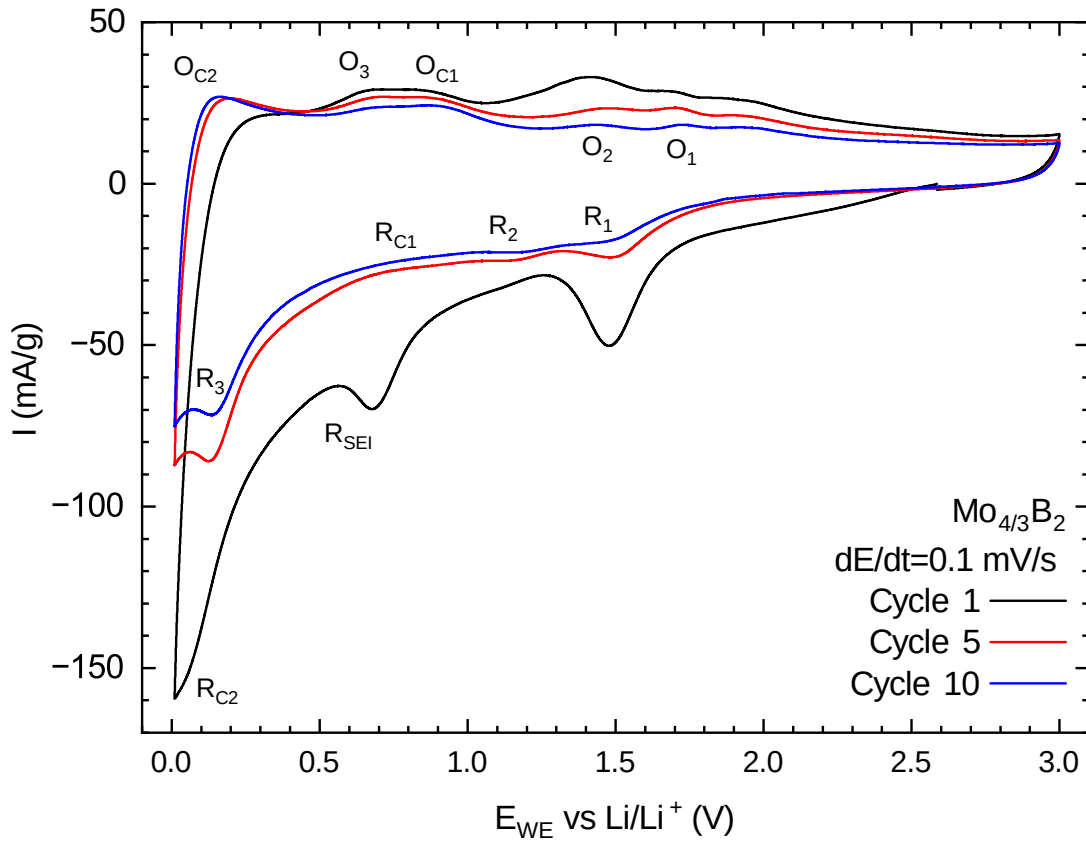


Figure 5.6: Cyclic voltammograms of cycle 1, 5 and 10 (in black, red and green, respectively) of $\text{Mo}_{4/3}\text{B}_2$ measured at a scan rate of 0.1 mV s^{-1} . The labels R/O represent distinct reduction and oxidation peaks.

the $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$ precursor, $\text{R}_{\text{C1}}/\text{O}_{\text{C1}}$ and $\text{R}_{\text{C2}}/\text{O}_{\text{C2}}$ correspond to the intercalation of Li-ions into CB, which is a constituent of the working electrode (see chapter 2.4). The origin of the other three redox pairs $\text{R}_{1/2/3}/\text{O}_{1/2/3}$ may be related to the MAB precursor material, which also exhibits three redox pairs. These are in the same voltage regions like the redox pairs of $\text{Mo}_{4/3}\text{B}_2$ and might be activated during the etching process. Another possible explanation for the origin of R_2/O_2 is related to the electrochemical activity of the MoB impurity. According to [69], MoB features a dominant redox pair in the voltage region of R_2/O_2 , which relates to intercalation processes of Li-ions into MoB. All in all, the CV of $\text{Mo}_{4/3}\text{B}_2$ exhibits several redox pairs corresponding to intercalation processes. It could not be identified, whether these correspond to insertion processes of Li-ions into $\text{Mo}_{4/3}\text{B}_2$ MBene phase, activated MAB phase or MoB impurity.

To evaluate the overall performance of the MBene, GCPL measurements were performed. Fig. 5.7(a) shows the specific capacity at a (dis)charging current of $I = 0.1 \text{ A g}^{-1}$ over the first 100 cycles. $\text{Mo}_{4/3}\text{B}_2$ exhibits an initial capacity of 614 mA h g^{-1} which drops to 320 mA h g^{-1} after the first cycle and saturates at 282 mA h g^{-1} at cycle 100. The electrode thereby exhibits an almost perfect Coulomb efficiency of $> 99 \%$.

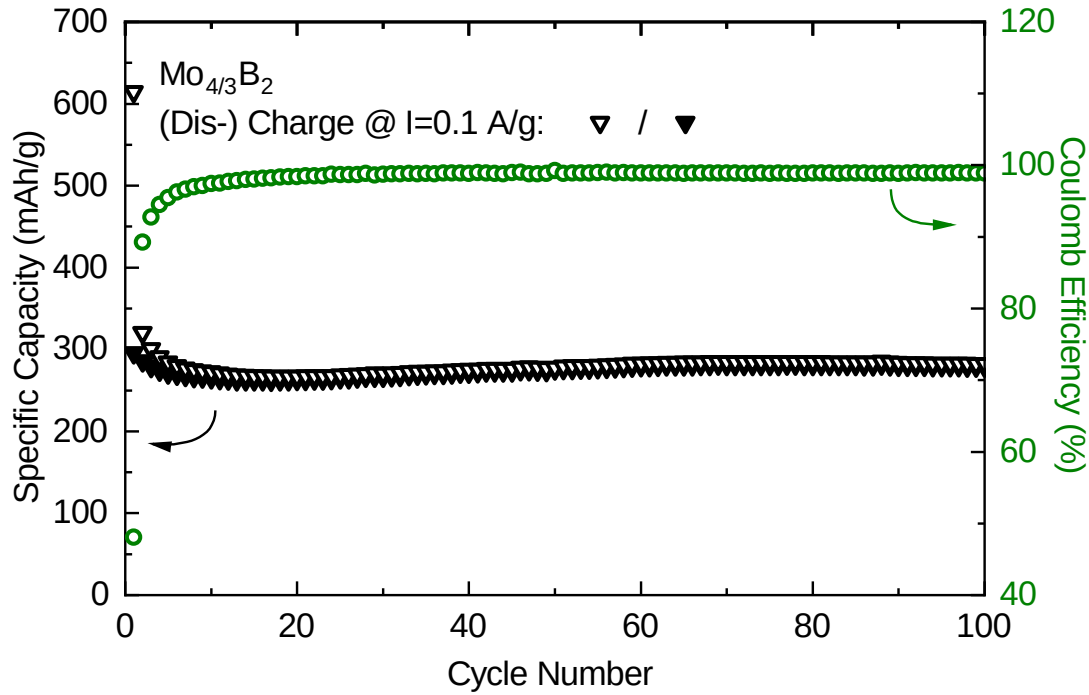


Figure 5.7: Specific discharge and charge capacities (black) of $\text{Mo}_{4/3}\text{B}_2$ electrodes at 0.1 A g^{-1} obtained in the voltage regime from 0.01 to 3 V and corresponding Coulomb efficiencies (green).

In GCPL measurements in Fig. 5.7(a) of $\text{Mo}_{4/3}\text{B}_2$, the fading in specific capacity after the first cycle can be assigned to SEI formation [30, 31]. Upon cycling, the specific capacity is very stable at 282 mA h g^{-1} , which equals to 1.32 electrons inserted in each structural unit in $\text{Mo}_{4/3}\text{B}_2$ (contribution of CB to the specific capacity was subtracted). Table 5.1 compares the specific capacity value of $\text{Mo}_{4/3}\text{B}_2$ in this work with the theoretical capacity and literature values. The theoretical capacity of $\text{Mo}_{4/3}\text{B}_2$ was calculated to be $C_{\text{theo}, \text{Mo}_{4/3}\text{B}_2} = 358 \text{ mA h g}^{-1}$, considering two electrons intercalated in each structural unit. The discrepancy of 2 electrons compared to 1.32 electrons inserted in each structural unit as measured, might originate from impurities in the sample. Residual MAX phase, AlF_3 and Li_3AlF_6 observed via XRD in Fig. 5.2 are electrochemically inactive but still have mass contributions, which decreases the effective specific capacity. Furthermore, there is no evidence that pure $\text{Mo}_{4/3}\text{B}_2$ MBene phase was synthesized properly. Comparing the MBene synthesized in this work with other MBenes from literature also shows the weak performance of $\text{Mo}_{4/3}\text{B}_2$. MoB [69] and Mo_2B_2 [68] MBenes exhibit at least twice as much specific capacity. As discussed above, the discrepancy is related to the poor synthesis process.

Table 5.1: The total specific capacity values after cycle 100 at a (dis-)charging current of 0.1 A g^{-1} and corresponding amount of inserted electrons per structural unit in different MBenes. The mass ratio of active material (AM), Carbon black (CB) and binder (PVDF) of the electrode is also indicated. The mass contribution of CB to the specific capacity was subtracted before calculating the amount of inserted electrons per structural unit. The values are compared to theory and literature.

Sample	Capacity (mAh/g)	AM:CV:PVDF	# Electrons
Theory	358	/	2
$\text{Mo}_{4/3}\text{B}_2$	282	70:20:10	1.32
Mo_2B_2 [68]	565	75:15:10	2.96
MoB [69]	600(20)	80:10:10	2.30

5.3 Conclusion for $\text{Mo}_{4/3}\text{B}_2$

This work presented first principle investigations on $\text{Mo}_{4/3}\text{B}_2$ MBenes as an anode material for LIBs using several physical and electrochemical characterization methods. The sample was synthesized by Dr. Peng Guo via the precursor material $(\text{Mo}_{2/3}\text{Y}_{1/3})_2\text{AlB}_2$ by selectively etching the Y and Al phase using a solution of $\text{HCl} + \text{LiF}$ as an etching solvent. The XRD pattern reveals that $\text{Mo}_{4/3}\text{B}_2$ consists out of several constituting parts, i.e. a lot of residual MAB phase that was not etched properly and impurity phases like MoB, LiF_3 and Li_3AlF_6 which were introduced during the etching process. While it was shown that the parental precursor material is only weakly electrochemically active, the MoB impurity is a MBene by itself showing strong electrochemical activity. The definite occurrence of pure $\text{Mo}_{4/3}\text{B}_2$ MBene phase could not be determined due to a missing (003) diffraction peak in the low angle range, which indicates an insufficient synthesis. SEM images of $\text{Mo}_{4/3}\text{B}_2$ show two phases, i.e. residual MAB phase and oval shaped particles with a coarse surface in a range of $1 \mu\text{m}$, probably an impurity. The expected accordion-like morphology similar to MXenes was not observed which again indicates an unsuccessful etching process. CV displayed several redox peaks, originating either from activated MAB phase, MoB impurity or $\text{Mo}_{4/3}\text{B}_2$ MBene. GCPL measurements revealed a stable specific capacity of 282 mA h g^{-1} which is approx. half of the capacity observed in similar MBenes in literature. This poor performance most probably originates from the insufficient synthesis process.

6 Summary

In this work, transition metal Carbides and Borides from the material class of MXenes and MBenes were studied with respect to their application potential as future anode materials for LIBs. Specifically, the impact of novel Mn-doping on V_2C MXenes, the usage of different etching solvents during the synthesis of Mn-doped V_2C MXenes, and first principle measurements on $Mo_{4/3}B_2$ MBenes were investigated. The samples were explored structurally and electrochemically using XRD, SEM, EDS, XPS, CV, GCPL and EIS.

In the first part of this work, the impact of $\sim 1\%$ Mn-doping on V_2C , i.e. Mn- V_2C , was investigated. The XRD patterns of both MXenes reveal a clear shift of the (002) diffraction peak to lower angles at $2\theta < 10^\circ$ compared to their precursor materials, demonstrating the successful synthesis of pure MXene phase. Mn- V_2C thereby exhibits a $> 10\%$ enlarged interlayer spacing compared to V_2C . Furthermore, XRD shows that both samples consist out of three constituting parts. These are (a) electrochemically active pure MXene phase indicated by the aforementioned emerging (002) diffraction peak, (b) electrochemically inactive residual MAX phase that was not etched properly and (c) electrochemically inactive impurity phases like Li_3AlF_6 and LiF introduced during the etching process. Subsequent GCPL measurements display a significant increase in specific capacity by more than 30% both at low and at high current densities for Mn- V_2C over V_2C . CV and GCPL potential profiles show same electrochemical behavior, showing that no new processes are taking place in the samples. A possible explanation for the increased capacity in Mn- V_2C could be different mass proportions of the constituting parts of the samples, which may lead to different specific capacities. Furthermore, the increased interlayer spacing of Mn- V_2C compared to V_2C increases Li-ion transport properties and lead to faster kinetics. Supporting this, EIS thereby revealed a reduced charge transport resistance by $> 25\%$ in Mn- V_2C .

In the second part of this work, the impact of the usage of different etching solvents during the synthesis of Mn- V_2C , i.e. $HCl + LiF$ or $HCl + NaF$, was investigated. The XRD patterns of Mn- $V_2C(LiF)$ and Mn- $V_2C(NaF)$ (according to which etching solvent was respectively used) reveal a clear shift of the (002) diffraction peaks to lower angles at $2\theta < 10^\circ$ compared to their precursor material, demonstrating the successful synthesis of pure MXene phase. Mn- $V_2C(NaF)$ thereby exhibits a much weaker pronounced peak indicating more residual MAX phase, compared to Mn- $V_2C(LiF)$. Furthermore, XRD shows that both samples consist out of three constituting parts. These are (a) electrochemically active pure MXene phase indicated by the aforementioned emerging (002) diffraction peak, (b) electrochemically inactive residual MAX phase that was not etched properly and (c) electrochemically inactive impurity phases $Li_3AlF_6/Na_5Al_3F_{14}$ introduced during the

etching process. Subsequent SEM images display a typical accordion-like morphology for both samples. While $\text{Mn-V}_2\text{C}(\text{LiF})$ features an wide open lamella structure, the structure of $\text{Mn-V}_2\text{C}(\text{NaF})$ looks more dense and closed with a high amount of $\text{Na}_5\text{Al}_3\text{F}_{14}$ on the sample surface. Following GCPL measurements display a significantly higher specific capacity in $\text{Mn-V}_2\text{C}(\text{LiF})$ by almost 50%. Explanations for the reduced specific capacity in $\text{Mn-V}_2\text{C}(\text{NaF})$ are a higher amount of electrochemically inactive residual MAX phase giving weight contribution, a more closed MXene structure with $\text{Na}_5\text{Al}_3\text{F}_{14}$ impurity on the sample surface hindering electrolyte penetration, and an increased charge transport resistance measured via EIS.

In the third part of this work, first principle measurements on $\text{Mo}_{4/3}\text{B}_2$ MBenes were investigated. The XRD pattern reveals that $\text{Mo}_{4/3}\text{B}_2$ consists out of two constituting parts, i.e. (a) lightly electrochemically active residual MAB phase that was not etched properly and (b) partly electrochemically active impurity phases like MoB , LiF_3 and Li_3AlF_6 which were introduced during the etching process. Due to a missing (003) diffraction peak in the low angle range, the definite occurrence of pure $\text{Mo}_{4/3}\text{B}_2$ MBene phase could not be determined, which indicates an insufficient synthesis. SEM images of $\text{Mo}_{4/3}\text{B}_2$ show two phases, i.e. residual MAB phase and oval shaped particles with a coarse surface. The expected accordion-like morphology similar to MXenes was not observed which again indicates an unsuccessful etching process. CV displayed several redox peaks, originating either from activated MAB phase, MoB impurity or $\text{Mo}_{4/3}\text{B}_2$ MBene. GCPL measurements revealed a stable specific capacity of 282 mA h g^{-1} which is approx. half of the capacity observed in similar MBenes in literature. This poor performance most probably originates from an insufficient synthesis process.

All in all, this work demonstrated that the material class of MXenes and MBenes exhibits a high variety of promising and tunable sample properties. But the performance of these materials used as future anode materials for LIBs significantly depends on a successful synthesis process that introduces less impurity phases, which decreases specific capacity. This concern needs to be optimized in the future.

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Declaration

I hereby confirm that I have written this thesis independently and have not used any sources or aids other than those specified.

A handwritten signature in black ink, reading "Tobias König". The signature is written in a cursive style with a prominent flourish at the end of the last name.

Heidelberg, 14th of July 2024