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submitted by

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Investigation of $\text{MoO}_x/\text{MXene}$ and WO_x/MXene composites as anode material for lithium-ion batteries

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Zusammenfassung

In der vorliegenden Arbeit wurden mehrere $\text{MoO}_x/\text{V}_2\text{C}$ - und $\text{WO}_x/\text{V}_2\text{C}$ -Nanokomposite auf ihre Verwendbarkeit als Anodenmaterial für Lithium-Ionen-Batterien untersucht. Zur physikalischen Charakterisierung wurden Methoden der Röntgenbeugung und der Rasterelektronenmikroskopie eingesetzt. Zur elektrochemischen Charakterisierung wurden zyklische Voltammetrie und galvanostatische Zyklen verwendet. Eine elektrochemische Charakterisierung eines MXenes, V_2C , wurde vorgenommen, um seinen Beitrag zu den Kompositen abzuschätzen. Eine reversible Kapazität von 213.2 mAh g^{-1} nach Zyklus 85 wurde gemessen. Die $\text{MoO}_x/\text{V}_2\text{C}$ -Charakterisierung zeigt, dass das Ausglühen die Morphologie der Probe veränderte, wie in SEM-Messungen zu sehen ist. Es veränderte auch das Komposit chemisch, reduzierte MoO_3 zu MoO_2 und beeinflusste die Kristallstruktur. Es zeigte sich auch, dass bei einem Verhältnis von 8 Teilen MoO_x zu 1 Teil das V_2C keine ausreichende Wirkung auf die Stabilisierung zeigte, während ein Verhältnis von 4:1 bessere Ergebnisse zeigte. Die beste Gesamtleistung wurde für das 4:1-Komposit gemessen, ausgeglüht bei 600°C , mit einer maximalen Kapazität von 708.1 mAh g^{-1} im 18. Zyklus. Um die Auswirkungen des Ausglühens einer TMO/MXene-Komposite weiter zu untersuchen, wurde außerdem ein zweites Komposit, nämlich $\text{WO}_x/\text{V}_2\text{C}$, untersucht, das ähnliche Ergebnisse zeigte. Das Ausglühen veränderte wiederum die Morphologie und Kristallinität sowie die chemischen Eigenschaften, wodurch WO_3 auf WO_2 reduziert wurde. Die beste Leistung wurde für den bei 600°C getemperten Verbundstoff mit einer maximalen Kapazität von 457.5 mAh g^{-1} im 6. Zyklus gemessen. Es wurde ferner bestätigt, dass das Ausglühen die elektrochemischen Eigenschaften der MXene-Verbundwerkstoffe positiv beeinflusst.

Abstract

In the present work, several $\text{MoO}_x/\text{V}_2\text{C}$ and $\text{WO}_x/\text{V}_2\text{C}$ nanocomposites have been investigated for their usability as anode material for lithium-ion batteries. Methods of x-ray diffraction and scanning electron microscopy have been used for the physical characterization. For the electrochemical characterization, cyclic voltammetry and galvanostatic cycling have been used. A electrochemical characterisation of an MXene, V_2C , has been made to estimate its contribution in the composites. A reversible capacity of 213.2 mAh g^{-1} after cycle 85 has been measured. The $\text{MoO}_x/\text{V}_2\text{C}$ characterization shows that annealing altered the morphology of the sample, as seen in SEM measurements. It also chemically altered the composite, reducing MoO_3 to MoO_2 , as well as affecting the crystal structure. It was also shown that, for a ratio of 8 parts MoO_x to 1 part, the V_2C did not show a sufficient effect on the stabilisation, whilst a ratio of 4:1 showed better results. The best overall performance was measured for the 4:1 composite, annealed at 600°C , with a maximum capacity of 708.1 mAh g^{-1} in the 18th cycle. Additionally, to further investigate the impact of annealing a TMO/MXene composite, a second composite, namely $\text{WO}_x/\text{V}_2\text{C}$ was investigated, showing similar results. The annealing again changed the morphology and crystallinity, as well as altering the chemical properties, reducing WO_3 to WO_2 . The best performance was measured for the composite annealed at 600°C , with a maximum capacity of 457.5 mAh g^{-1} in the 6th cycle. It was further verified that annealing positively affects the electrochemical properties of the MXene composites.

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1 Introduction

The society relies upon the portability and use of modern high-end devices or other factors, such as the feasibility of renewable energies or the ever growing demand of e-mobility. All of those technologies hinge on one common thing: The necessity of improved energy storage systems [1]. In particular, Lithium-ion batteries (LIBs) are decisively interesting for that application, due to their high energy density and long cycling stability [2]. LIBs are based on the reversible electrochemical storage of Li^+ -ions into a broad variety of electrode materials. Furthermore, there are multiple ways to store those Li^+ -ions, notably intercalation and conversion [4]. For the intercalation, Li^+ -ions diffuse into free spaces in the crystal lattice of the anode material, which limits the total capacity. For the conversion, different phases with different properties, altering the material chemically and physically. Whilst having a higher theoretical capacity, it also has a lower stability, due to degradation of the host material. One of the ways to improve those rates are through the use of better novel anode materials [3]. The goal is to develop such materials that outperform previous materials in capacity, longevity and manufacturing cost. Commercial LIBs use graphite as the anode material. Graphite possesses a comparatively low theoretical capacity of 372 mAh g^{-1} , since the main storage mechanism used is the intercalation of lithium ions. Recent research suggests the usage of conversion-type transition metal oxides (TMOs), such as MoO_2 with a theoretical capacity of 838 mAh g^{-1} [31] or WO_3 with a theoretical capacity of 693 mAh g^{-1} [32]. However, due to the nature of the conversion reactions, the structural stability of TMOs is limited, which leads to a weak cycling performance and the degradation of the host material [5]. The ion and electron conductivity is reported to be low aswell, which ultimately leads to pure TMOs not being suitable as an anode material. A way to improve their capacity retention is by incorporating TMOs into a structurally stable host material [6]. One promising candidate are the 2D MXene nano-sheets, discovered in 2011 by Naguib et al. [7], those having an excellent cycling stability and capacity, due to high conductivity and a favorable structure [3]. MXenes are the product of selectively removing the A layers from a MAX-type precursor, resulting in an accordion-like lamellae structure. Specifically V_2C , made from the precursor V_2AlC is of interest. In this work, two specific TMO/MXene composites, namely $\text{MoO}_2/\text{V}_2\text{C}$ and $\text{WO}_3/\text{V}_2\text{C}$ was investigated for the potential use as an anode material for LIBs. Furthermore, the effect of annealing at different temperatures, as well as different mass ratios have been investigated. In the quest to find better anode materials for LIBs, the morphology and crystallinity of a given material with the electrochemical properties, is an important factor. Knowing those relations is important for the optimization of those materials.

In the following, the fundamentals are going to be outlined, including the electrochemical basics needed and an introduction to the materials used. This is followed by an introduction on the experimental methods and procedures. In Chapter 3, the results are going to be presented, with an characterisation of the pristine MXene material and the two composites. This is followed by a final summary of the results in chapter 4.

2 Fundamentals

2.1 Electrochemistry

The idea of electrochemical energy is converting chemical energy into electrical energy and vice versa. A realization of this is through the galvanic cell. A galvanic cell consists of two half-cells, each consisting of an electrode, and an ion-conducting electrolyte [8]. The electrodes are connected electronically. The electrodes consist of at least one electrochemically active redox pair, generally described through the following reaction:



Ox and Red stand for the oxidized and reduced state of the species and n is the number of electrons involved in the reaction. One speaks of a secondary cell, if this reaction is reversible. Per definition, the oxidized electrode is the anode, while the reduced electrode is the cathode [9]. The potential of an cell is given by the difference of the potentials of the used half-cells, where as those are given by their standard potential measured with a reference electrode. The potential of a half cell can also be calculated through the Nernst-equation:

$$E = E_0 + \frac{RT}{nF} \cdot \ln \left(\frac{a_{\text{Ox}}}{a_{\text{Red}}} \right) \quad (2)$$

Where E_0 is the standard electrode potential for a given species, R is the universal gas constant, T is the temperature, F is the Faraday constant and $a_{\text{Ox/Red}}$ are the activities of the reacting couple [8][10]. To recharge a battery, electrons have to be provided for the ions to be reduced and then diffuse back into the neutral state. This is realized by applying a voltage, opposite to the voltage provided by the battery [9][11]. It is noteworthy, that only the basic electrochemical mechanisms are addressed in this work. For example, the diffusion through the electrolyte has been neglected.

Lithium ion batteries A way to realise secondary cells is the Lithium-ion battery (LIB). The following describes the two storage mechanisms that occur in this work. Figure 2.1 shows a schematic.

Intercalation One way for lithium ions to accumulate into an active material is intercalation, where the free ions diffuse into free spaces in the crystal lattice. Ideally, the crystal structure stays intact and the spatial expansion is kept to a minimum. This type of lithium storage comes with a high degree of reversibility, but at the cost of a lower capacity, as there usually is only one Li^+ -ion per formula unit stored [11][12].

Conversion Another way for lithium ions to accumulate into the active material is conversion, where the active material is chemically and structurally converted. Thus, new phases with different properties emerge. One pro of that is the increased capacity, as

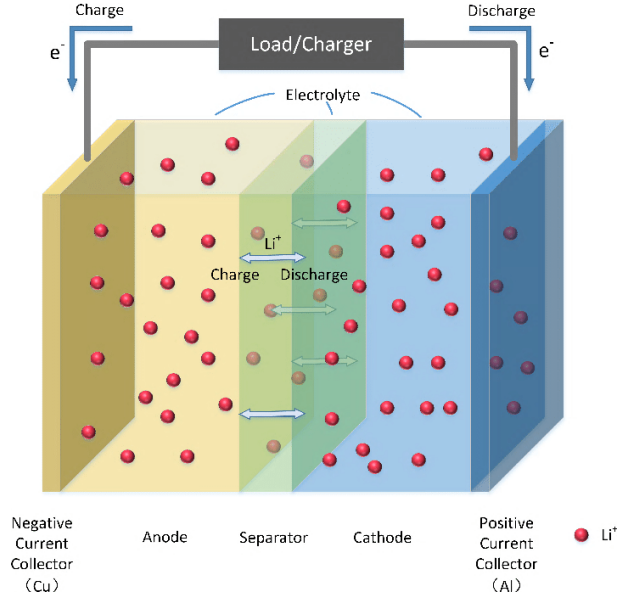
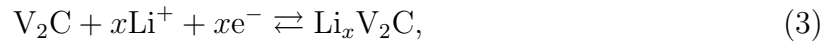


Figure 2.1: Schematic showing a LIB [20]

more than one Li⁺-ion is stored per unit, at the cost of a greatly decreased cycling stability, due to the structural changes and limited reversibility. The volume of the crystal can also greatly change, which further decreases stability. Furthermore, the materials get fractioned over time into electrochemically inactive phases.[5]

MXenes The MXenes are a new family of layered 2D nanomaterials first discovered by Naguib et al. in 2011 [7]. An interest for those materials to be used in LIB's has been seen early, due to the enormous potential. MXenes are the product of removing the A layer of a MAX precursor (e.g. by using hydrofluoric acid and subsequent sonication). M denotes an early transition metal (e.g. Mo or W), A denotes an element from the 13th or 14th group (e.g. Al or Si) and X denotes either C or N. In figure 2.3 three possible MAX phases are shown, with the subsequent MXenes that emerge from them after the removal of the A layer. In this case, the 211 MAX phase is relevant for this work. MAX phases have no particular importance in LIB's, where as MXenes are very interesting due to their large specific surface area useful for intercalation and accomodation of redox sites, as well as their high conductivity. Figure shows a M₂X monolayer with sixfold symmetry and a rhombic unit cell. The M₂X monolayer consists of a X sublayer enclosed by two M sublayers. The empty sites four extra bonds are represented with A and B in figure 2.4.

In this work, the MXene used in both composites is V₂C, synthesized by the precursor V₂AlC. The theoretical specific capacity of V₂C is 940 mA h g⁻¹ [33]. The de-/lithation reaction is assumed to be the following:



Moreover, the diffusion barrier for an isolated Li atom is very low, enabling large dis-/charge rates [33]. In summary, MXenes, more specifically V₂C, show a great cycling performance due to the high mechanical stability and high conductivity. But, the theoretical capacity has not been achieved yet. The specific capacities can be achieved by forming composites with e.g. transition metal oxides, to maximize positive aspects of

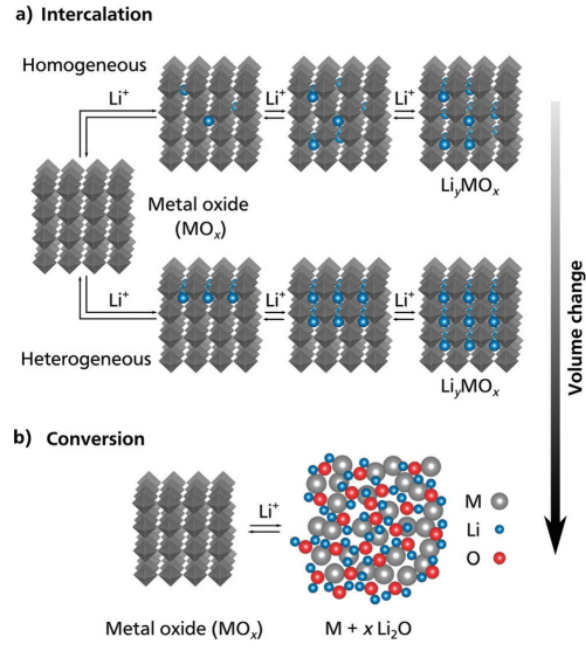


Figure 2.2: Schematic showing the two lithiation mechanisms[21]

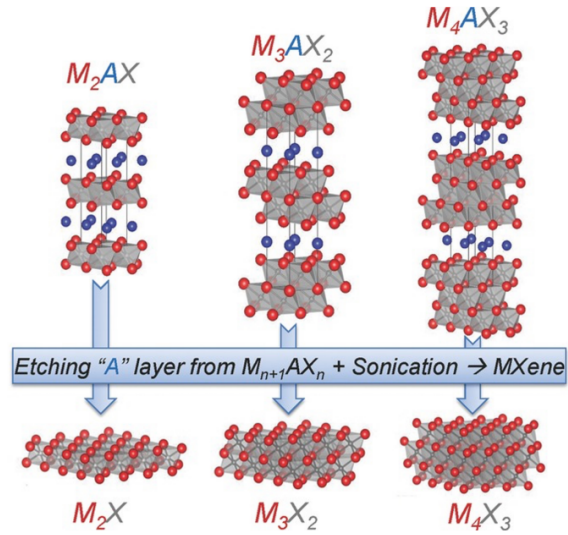


Figure 2.3: Synthesis of pristine MXene monolayers, from 211, 312 and 413 MAX phases [25].

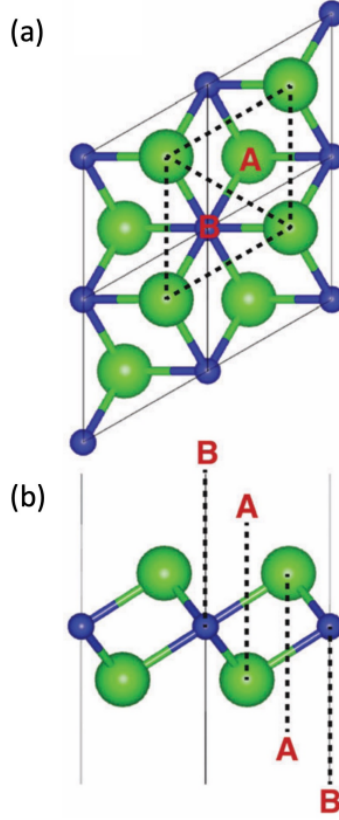
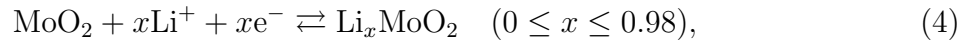


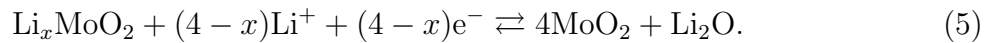
Figure 2.4: Synthesis of pristine MXene monolayers, from 211, 312 and 413 MAX phases [24].

each, while minimizing the negative aspects.

MoO₂ as an anode material One of the transition metal oxides investigated in this work is MoO₂, used to form a composite with the V₂C. It is proclaimed to be a promising anode material, due to a high theoretical capacity of 838 mA h g⁻¹, a reasonable price and good environmental compatibility. The reason, why one would be interested in that composite is that MoO₂ has a low electrical resistance compared to most transition metal oxides, which usually show a poor conductivity. The primary storage mechanisms here are intercalation and conversion. The intercalation follows the following formula:



while the conversion follows the following formula:



On top of that, as shown in figure 2.5, the crystal structure consists of tunnel usable for Li⁺-ion transport and intercalation. We are adding V₂C to it to increase the structural integrity and cycling performance, while decreasing the amount of conversion reactions happening, which show a worse cycling performance due to the nature of that reaction. The formation of the composite with the MXene hopes to increase the stability and conductivity of MoO₂.

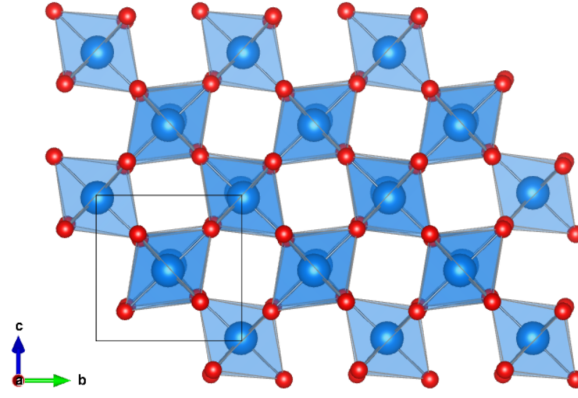
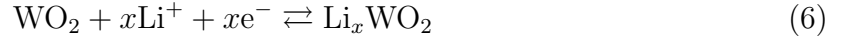
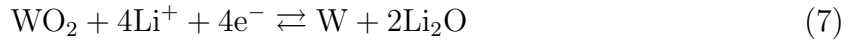


Figure 2.5: Crystal structure of MoO_3 [22]

WO_2 as an anode material The second transition metal oxide used in this work is WO_2 , also used to form a composite with the V_2C . It is commonly used as a photocatalyst. The pure metal oxide suffers from a low conductivity and low cycling stability, similar to the MoO_2 , yet with a high theoretical capacity of 693 mA h g^{-1} . The intercalation follows the following formula:



while the conversion follows the following formula:



Similar to MoO_2 , the addition of V_2C hopes to increase the cycling stability and conductivity.

2.2 Experimental procedures

X-ray diffraction (XRD) X-ray diffraction is used for the physical characterization of a given sample. Conclusions about the crystal phases, lattice parameters and quality of a composite can be drawn from the measurements. Due to the diffraction from parallel atomic planes, if the distance d and more so the wavelength λ of the x-rays are chosen right, only then is there constructive interference. For that to happen, the path difference $2\Delta x$ has to be equal to a integer multiple of the wavelength λ . With $d \sin(\theta) = \Delta x$, we can formulate Bragg's law:

$$n\lambda = 2d \sin(\theta), \quad n \in \mathbb{N}, \quad (8)$$

which is the condition for constructive interference. Another condition is that $\lambda \leq 2d$, the wavelength has to be small enough to resolve the structures. Usually, the Debye-Sherrer method is used, where fine-grained polycrystalline samples are irradiated with monochromatic light. The reflections that occur due to the Bragg-diffraction ideally enclose a ring due to the conic shape of the of the reflected rays. Those rings are unique to each angle 2θ , so the intensity of each ring can be plotted against the angle 2θ . The result is a diffractogram which provides specific information about the crystal and it can be easily compared to known data [12][14].

The XRD measurements were performed by Mrs. Glas at the Institute of Geosciences at Heidelberg University with a Bruker D8 Advance ECO diffractometer with Bragg-Brentano geometry and an SSD160 detector. The used x-rays were generated with a x-ray tube with a copper anode operated at 30 kV and a current of 33 mA. The range of 2θ is between 10° and 70° . For the analysis, the obtained data has been analyzed using "Match!", an analysis software for powder diffraction.

Scanning electron microscopy (SEM) This is used to investigate the morphology of a given sample. A focused electron beam is diverted onto the sample, where the electrons interact with the surface. There is a distinction made between two different scattering processes: Low energy secondary electrons and backscattered electrons. The low energy secondary electrons arise due to elastic scattering within the sample through which, secondary electrons emerge from within the surface of the sample. The signal produced from these depict the topology of the given sample. On the other hand, the backscattered electrons are those from the electron beam, being scattered inelastically from the surface. Those allow a conclusion to be made, about the chemical composition of the material. The ammount of backscattered electrons increases with the atomic number of the atom. Those also give us crystallographic information, due to electron channeling [13].

The SEM measurements were performed by Peng Guo at the Institute of Physical Chemistry at Heidelberg University, using a scanning electron microscope LEO 1530 Gemini SEM (Zeiss).

Cyclic voltammetry With the Cyclic voltammetry (CV), one can investigate the electrochemical mechanisms of a given material. A triangular signal with a certain scan rate $\nu = \frac{\partial V}{\partial t}$ is applied to the battery and the current is measured. In certain potential ranges, electrochemical reactions occur, which result into characteristic current peaks visible in the voltammogram. A positive current corresponds to a oxidation of the material, a negative current to a reduction. If a oxidation peak and a reduction peak exist together as a pair, one can deduce the reversibility of a certain process. In a diffusion dominated process, the amplitude of the peak is proportional to the square root of the scan rate

[15][16].

Galvanostatic cycling Galvanostatic cycling with potential limit (GCPL) is a technique used to determine the cycling performance and cycling stability of a given cell. It uses a constant current while measuring the voltage. One can determine the specific capacity by integrating the current over the elapsed time and standardize it over the active mass.

$$Q_{spec} = \frac{1}{m} \int_{t_1}^{t_2} I(\tau) d\tau \quad (9)$$

Furthermore, a measure for the reversibility of a electrochemical process is the coulombic efficiency which is given by the following ratio:

$$\eta_C = \frac{Q_{delith}}{Q_{lith}} \quad (10)$$

The theoretical specific capacity is given by Faraday's law:

$$Q_{theo} = \frac{zF}{M} \quad (11)$$

With z being the number of exchanged electrons, F as Faraday's constant and M as the molar mass of the active material [17][18][19].

Both processes are performed on a Biologic potentiostat (VMP3, VSP, BCS-805) in combination with the EC-Lab software. Each measurement was preceded by a open-circuit voltage (OCV) routine, measuring the open-circuit voltage of a cell, thus the actual measurements start in a chemical equilibrium state. A script written by Viktor Adam for OriginPro was used to process the measured data.

Preparation of the electrodes For the measurements, electrodes containing the material to be examined are prepared. In an amber glass vial, seven parts of the material is mixed with two parts by weight of polycrystalline carbon (carbon black) as a conductive additive and one part by weight of polyvinylidene difluoride (PVDF) as a binding agent. N-Methyl-2-pyrrolidone (NMP) acts as a solvent and is added afterwards. The slurry is then stirred for around 24 hours, with the help of a magnetic stir bar and afterwards dried in a vacuum oven at 65°C for around 3-9 hours or until the slurry reached a coat-able consistency. In the meantime, three copper meshes, with a diameter of 10mm, were weighed for each sample and afterwards coated with the more viscous slurry. The coated copper meshes then get dried for 24 hours, then weighed again to determine the mass of the active material. After flattening the electrodes with an hydraulic press and die, the most suitable electrode gets used for the battery assembly.

Battery assembly To standardize the measurement, a coin battery with certain specifications is assembled in an argon filled glovebox ($c(\text{H}_2\text{O}) < 10$ ppm, $c(\text{O}_2) < 10$ ppm). A stainless steel casing (SS304/SS316) of type CR2032 serves as the housing for the coin battery. A wave spring in the bottom case provides internal pressure, as a 0.5 mm thick stainless steel spacer acts as a current collector. On that spacer, lithium is stamped on

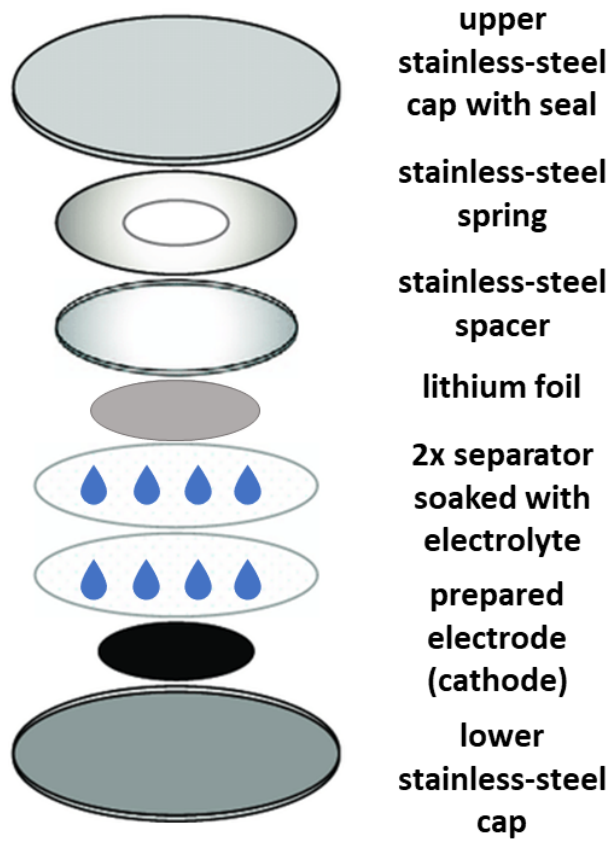


Figure 2.6: Schematic of a cell[23].

to act as a negative electrode and two glass fiber separators are added on top. Those are each soaked with 65 μl of an electrolyte solution (1M LiPF_6 in 1:1 ethylene carbonate and dimethyl carbonate). The prepared electrode is added on top and the battery is closed with the top case and then pressed and sealed with the MSK 640-G press manufactured by TMAX using a pressure of 31.2 MPa.

3 Results and Discussion

Initially, the pristine MXene is characterised physically and electrochemically. Afterwards the composites are characterised and the effect of the annealing temperature and the mass ratio of TMO to MXene is studied. All samples were prepared by Peng Guo.

3.1 Pristine V_2C

Prior to the investigation of the composites, a characterisation of the MXene is made, which is part of both composites. To verify the substance to be V_2C , and to investigate its purity, an XRD measurement has been done by Peng Guo. The diffractograms of the synthesized MXene and its precursor are shown in figure 3.1. The precursor V_2AlC shows a large characteristic peak at 13.6° and one at 41.2° . For the MXene, a new peak at around 8.6° emerged, belonging to the (100) plane, and the lammellae structure. Another two peaks emerged at 21.2° and 21.5° . The remaining peaks are those of the precursor, shifted slightly to the left, which indicates a possible decrease of the interlayer spacing.

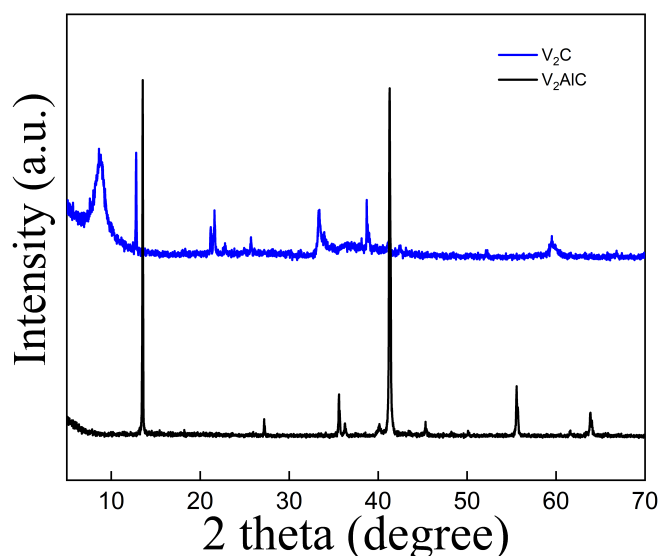


Figure 3.1: XRD pattern of V_2C and its precursor V_2AlC , made by Peng Guo.

The SEM pictures in figure 3.2 give us insight about the morphology of V_2C . It consists of a lamellae structure with the layers being about several nanometers thick. Those layers add up to bigger structures with a size of up to $10\text{ }\mu\text{m}$. There are also some extraneous material visible in between the layers, which is common to see with MXenes.

In order to electrochemically characterize the pristine material, a CV measurement of the

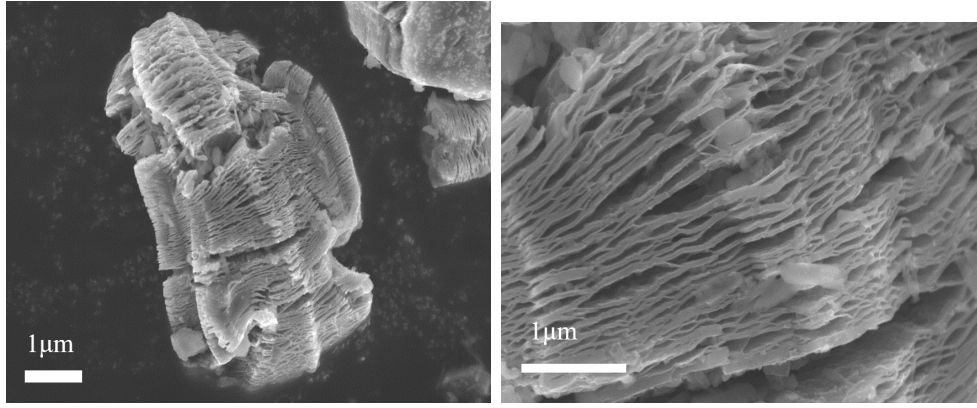


Figure 3.2: SEM images of V_2C in two different magnifications, made by Peng Guo.

sample has been performed, at a scan rate of 0.05 mV s^{-1} in a potential range of $0.01 \text{ V} - 3.00 \text{ V}$. The data are shown in figure 3.3. The OCV was 3.2 V . During the initial lithiation, two irreversible processes occur at 2.87 V and 2.45 V . Those peaks could be attributed to impurities within the MXene, as they do not show up in the literature, according to Fanfan Liu et al. [27]. The redox pairs at $1.86/2.50 \text{ V}$, $0.98/1.24 \text{ V}$ and $0.81/0.58 \text{ V}$ could be attributed to the de-/intercalation of the lithium ions into the V_2C . The peak R_{SEI} at 0.70 V , which occurs only on the first cycle, could be attributed to the irreversible formation of the SEI. It is notable that this peak merged with R_3 for the first cycle. The peaks R_c and O_c at $0.02/0.18 \text{ V}$ appear due to the lithium ions de-/lithiation into the carbon black. Overall, the electrochemical activity increases over time, after the first cycle, probably due to the interlayer spacing getting enlarged over time, as well as due to enhanced electrolyte infiltration. Overall the CV is mostly in agreement with Fanfan Liu et al., barring the first two peaks of the first reductive sweep [27].

For further investigation a GCPL measurement has been performed by Peng Guo, shown in figure 3.4. The measurement has been performed at a current density of 100 mA g^{-1} in a potential range from 0.1 V to 3.0 V . The initial lithiation capacity amounts to 327.6 mAh g^{-1} and the delithiation capacity amounts to 169.8 mAh g^{-1} with a coulombic efficiency of 51.8% . The huge discrepancy between the initial lithiation and the delithiation capacity is attributed to the irreversible formation of the SEI. After the fourth cycle, the capacity rapidly declined to 182.2 mAh g^{-1} . The capacity steadily rises up until 213.2 mAh g^{-1} in the 85th cycle. This increase, as stated before, could be due to the increased interlayer spacing and enhanced electrolyte infiltration [27].

Overall, the physical characterisation shows that the synthesis of V_2C has been successful, albeit with some impurities, which was to be expected, due to the etching method. The layered structure was confirmed with the SEM measurements. It should be noted, that the MXenes are a relatively recent field and still needs to be explored more. The CV measurements show little to no irregularities except the irreversible peaks in the beginning. Those could be due to impurities or some other unknown processes. The GCPL measurement shows a reversible capacity of 182.2 mAh g^{-1} up to 213.2 mAh g^{-1} , in agreement with Fanfan Liu et al. [27].

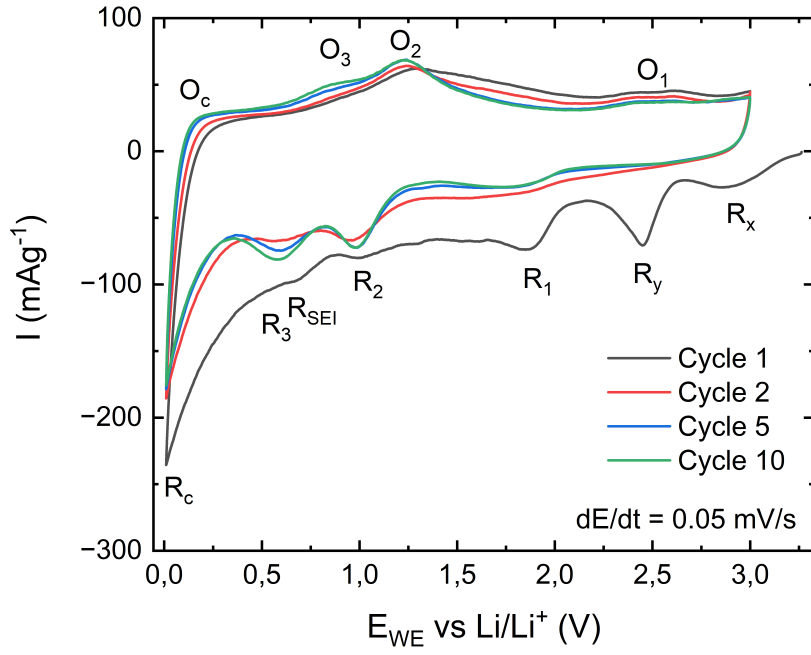


Figure 3.3: CV of pristine V_2C in the 1st, 2nd, 5th and 10th cycle, recorded in the voltage range of 0.01 V - 3.00 V at a scan rate of 0.05 mV s^{-1} .

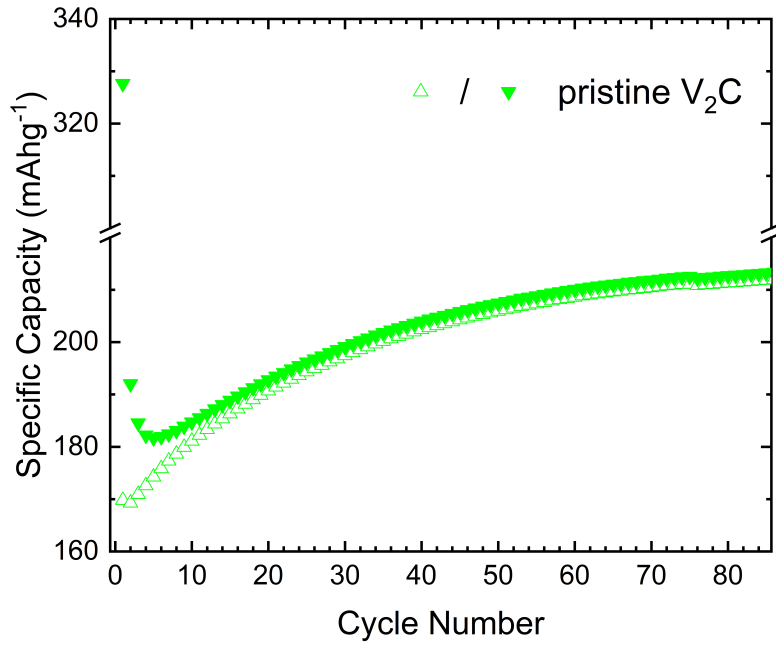


Figure 3.4: GCPL of pristine V_2C recorded in the voltage range of 0.01 V - 3.00 V at a current density of 100 mA g^{-1} .

3.2 $\text{MoO}_x/\text{V}_2\text{C}$

In this chapter, different composites of MoO_x and V_2C will be characterized. In this work, the mass ratio is varied as well as the annealing temperature. The effect of the variation of the parameters was investigated physically and electrochemically and the suitability of a given sample used in a battery was investigated.

Variation of the annealing temperature

In the following, the influence of the annealing temperature will be investigated. The samples provided have been annealed at two temperatures, namely 400°C and 600°C . For a comparison, the non-annealed samples are investigated as well. In total, 6 samples are investigated here.

The XRD patterns of all samples used are presented in figure 3.5. The peaks of the non-annealed composite with a mass ratio of 4 to 1 closely match those of the MoO_3 , as well as the major peak of the V_2C at around 8.2° , which indicates that the composite is indeed $\text{MoO}_3/\text{V}_2\text{C}$. This is expected, as h- MoO_3 was used to synthesize the composite. The 8 to 1 non-annealed sample only shows two peaks, one at 8.1° and a broad peak at 25.8° . Those match the main peaks of MoO_3 and V_2C . Due to the absence of other peaks, one may conclude that the sample is mostly amorphous and only the most significant structures, such as the lamellae structure are visible. For the annealed 4:1 composites, the peaks resemble the MoO_2 peaks, indicating that during the annealing process, MoO_3 got reduced to MoO_2 , changing the crystallinity of the sample. The V_2C peaks are barely

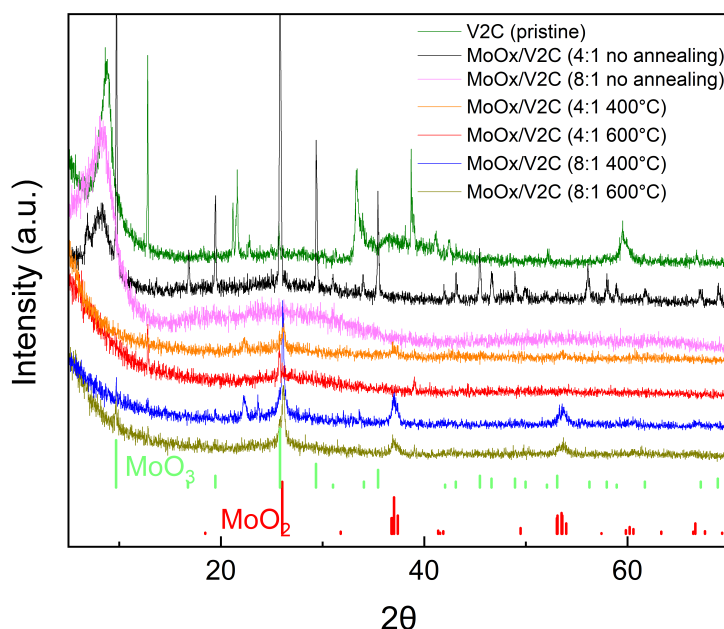


Figure 3.5: XRD patterns of different $\text{MoO}_x/\text{V}_2\text{C}$ composites, made by Peng Guo.

visible, notably at 12.8° and the main peak is not visible. This may indicate that the V_2C got filled with MoO_2 . And due to the low intensity of the peaks, one could conclude

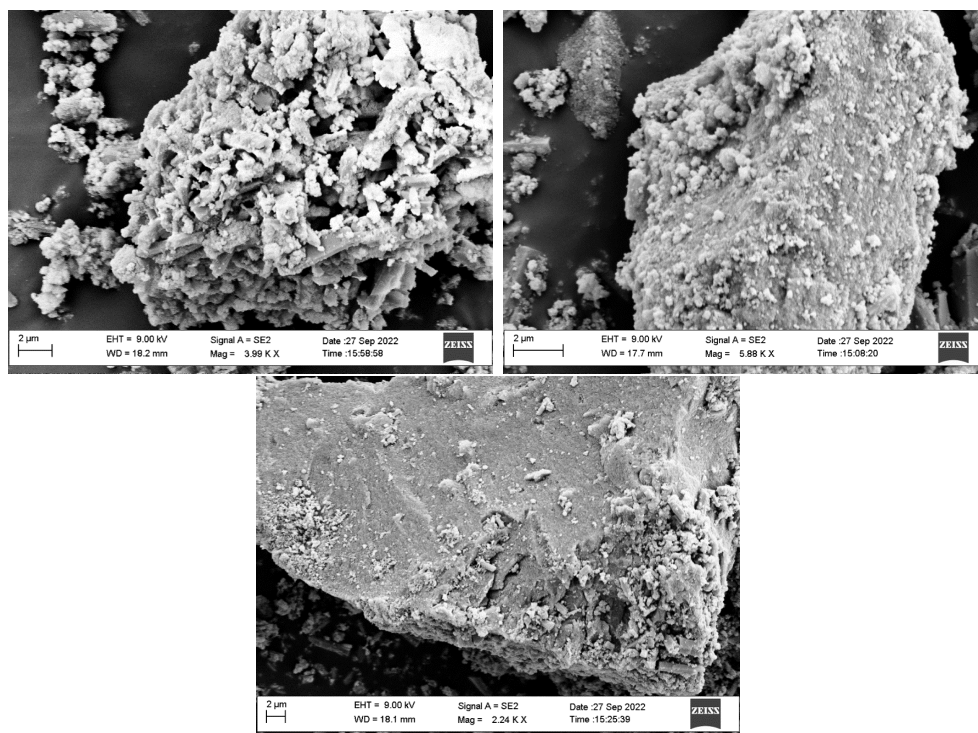


Figure 3.6: SEM pictures of different 8:1 $\text{MoO}_x/\text{V}_2\text{C}$ composites, top: non-annealed, middle: annealed at 400°C , bottom: annealed at 600°C . Images made by Peng Guo.

that the V_2C is saturated. There are few differences between the annealing temperatures, notably the peak at 39° for the 600°C composite, which doesn't appear for the 400°C composite, belonging to the V_2C . For the 8:1 composites that have been annealed, the main MoO_2 peaks are identifiable, in addition with some V_2C peaks that are more pronounced than on the 8 to 1 sample. Notably, 22.3° and 22.7° for the 400°C sample. Due to the higher intensity, it can possibly be concluded that the V_2C is oversaturated with the MoO_2 and that the excess MoO_2 could be agglomerated on the surface.

The following 3 composites have a mass ratio of 8 parts MoO_x to 1 part V_2C . For a further understanding of the composite, SEM pictures have been taken. Figure 3.6 shows the images. In the non-annealed sample, the V_2C lamellae structure is visible, as well as a large amount of the h- MoO_3 nanorods, used in the synthesis of the composite. For the sample annealed at 400°C , the MXene lamellae are not visible anymore, perhaps due to the annealing process. Further details are not known. Same applies for the 600°C sample, where the MXene structure is barely visible. The MoO_2 seems to be agglomerated onto the surface and inside the MXene, but with an excess of MoO_2 forming on the surface.

The CV data are shown in figure 3.7. The scan rate is set to 0.05 mV s^{-1} . The OCV is 3.2 V. For the composite annealed at 400°C , one can see some electrochemical activity from the MoO_2 . In the first cycle, at 2.65 V an irreversible process happens. At 1.50 V the first reductive peak R_1 happens, which shifts to 1.56 V in the next cycles. Together with O_1 , it forms a pair which could be attributed to the MoO_2 , as it does not appear on the CV plot for the V_2C 3.3, as well as in other papers [28][29][31]. The second peak R_2 is located at 1.21 V in the first cycle and 1.26 V in subsequent cycles. Together with the peak O_2 at 1.43 V it forms a pair which can be attributed to the intercalation of

Li-ions into the V_2C , as it overlaps with the peaks seen in the plot for the pristine V_2C 3.3. R_{SEI} at 0.69V is due to the irreversible formation of an SEI, R_3 is very shallow and shifts between 0.39 V in cycle 2 to 0.15 V in cycle 10. It does not have a visible belonging oxidation peak though. This can be attributed to the conversion of the material according to [28][29]. As before, R_c/O_c at the lower end is attributed to the lithiation of Li-ions into the carbon black. The capacity slowly increases per cycle, after the first cycle. This could be due to the increasing interlayer spacing or enhanced electrolyte infiltration, similar to the pristine V_2C . For the sample annealed at 600°C, a similar trend can be seen, with more pronounced peaks at R_1/O_1 and R_2/O_2 occurring due to the intercalation of the lithium-ions. Again with irreversible processes happening during the first cycle and R_3 not having a visible direct partner to form a pair, rather O_3 being dispersed over the whole charging cycle. The non-annealed composite shows less electrochemical activity in comparison, only showing few reversible peaks. At 1.39 V a peak occurs due to the deintercalation into the MXene. R_c and O_c are due to the added carbon black. The peak at 1.97 V indicates an irreversible process which is unknown. Overall, the influence of annealing is clearly visible in the CV diagrams, as more electrochemical activity is happening in the annealed samples.

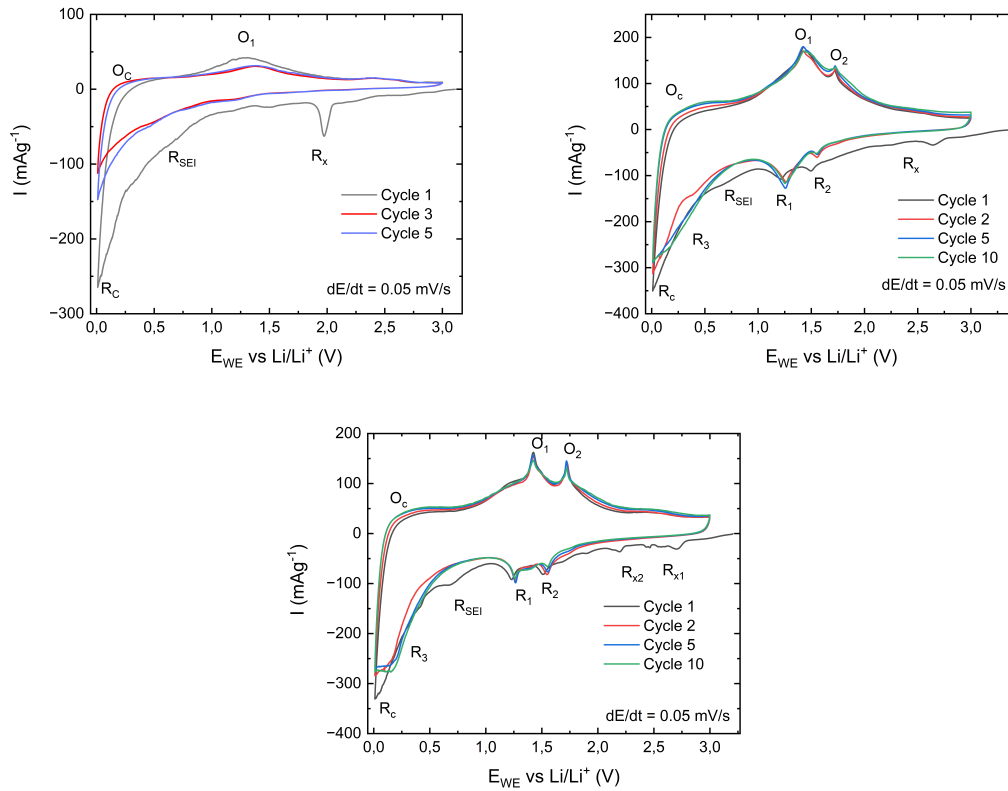


Figure 3.7: CV measurement of 8:1 MoO_3/V_2C in the 1st, 2nd, 5th and 10th cycle, recorded in the voltage range of 0.01 V - 3.00 V at a scan rate of 0.05 mV s⁻¹. Non-annealed left, 400°C right, 600°C bottom.

Next up are the GCPL measurements, to further investigate the cycling stability and reversible capacity of the composites.

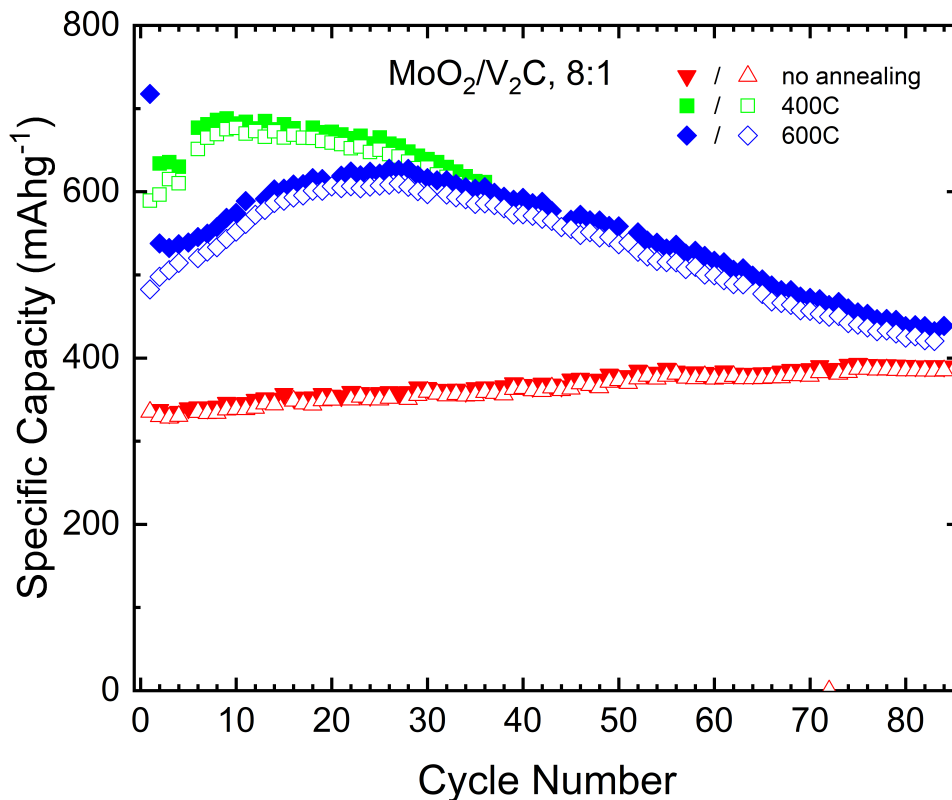


Figure 3.8: GCPL of 8:1 $\text{MoO}_2/\text{V}_2\text{C}$ recorded in the voltage range of 0.01 V - 3.00 V at a current density of 100 mA g^{-1} .

For the non-annealed sample, the reversible capacity is 329.9 mAh g^{-1} in cycle 2. The capacity slowly increases during cycling up to 384.9 mAh g^{-1} in cycle 84. For the composite annealed at 400°C , the capacity in cycle 2 is 634 mAh g^{-1} increasing up to 688.1 mAh g^{-1} in cycle 7 and decreasing to 611.6 mAh g^{-1} in cycle 36. Only the first 36 cycles are shown, due to the original measurement being interrupted and the data being corrupted by that. The capacity of the 600°C composite increases from 532.5 mAh g^{-1} in cycle 3 to 627.7 mAh g^{-1} in cycle 28, decreasing afterwards to 438.7 mAh g^{-1} in cycle 84. The annealed composites do have an overall higher capacity, yet a worse stability. This can be traced back to the structural degradation of the host material caused by the conversion reactions of the MoO_2 , whilst the non-annealed composite increases its capacity over time, as the interlayer distance gets bigger and the electrolyte infiltration increases.

The effects of annealing on the composite $\text{MoO}_x/\text{V}_2\text{C}$ with a mass ratio of 8:1 were investigated. In the XRD analysis, it was shown that the TMO reduced from its original state of MoO_3 to MoO_2 . The annealing process improved the crystallinity of the composite, as the non-annealed sample was mostly amorphous, with only the main V_2C peak and main MoO_3 visible. The disappearing of the main V_2C peak at around 8.2° in the annealed samples may be due to the V_2C getting saturated with the MoO_2 during the annealing process. The SEM pictures show similar results, as the h- MoO_3 is agglomerated on top of the V_2C rather than inside the V_2C . For the annealed samples, an agglomeration is still visible, yet the V_2C structure disappeared. This also leads to the conclusion, that

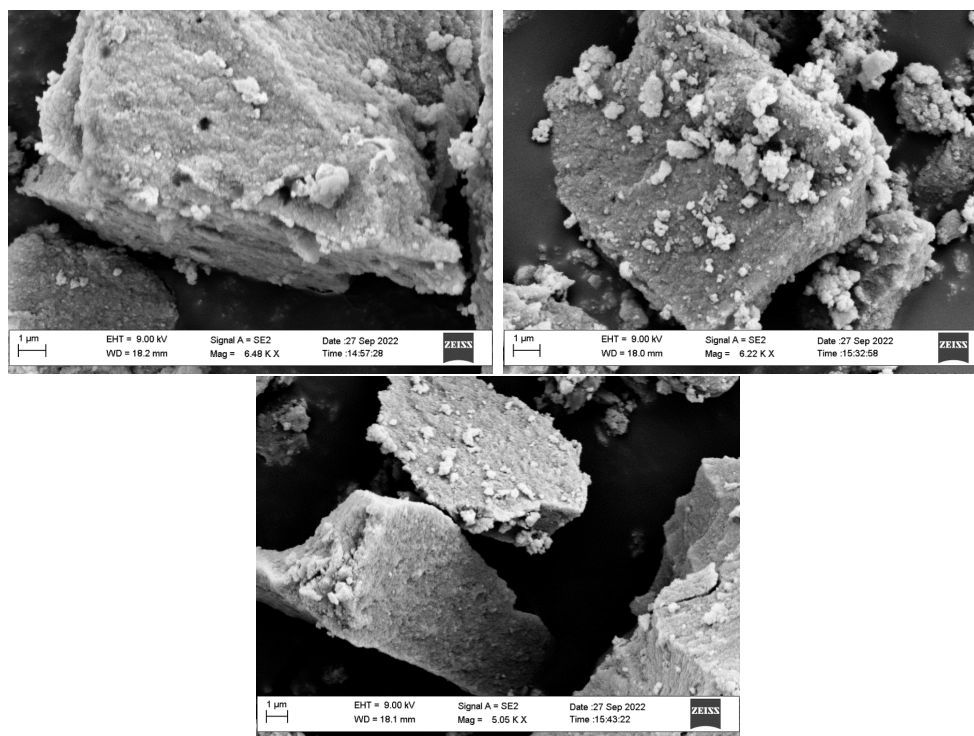


Figure 3.9: SEM pictures of different 4:1 $\text{MoO}_x/\text{V}_2\text{C}$ composites, top: non-annealed, middle: annealed at 400°C , bottom: annealed at 600°C . Images made by Peng Guo.

the V_2C is saturated with MoO_2 and that the excess has agglomerated onto the surface. The CV measurements shown in Figure 3.7 show characteristic peaks that are superimposed between the pristine V_2C and the MoO_x . The peaks could be assigned accordingly. Additionally, the GCPL measurements 3.8 show that the annealed composites show a higher capacity at the cost of stability, especially for the composite annealed at 600°C . The positive effect of annealing can be confirmed, but the contribution of the MXene seems to be lacking. For further investigation, a higher amount of MXene is going to be added to the composite.

To increase the stability, more V_2C has been added, making the mass ratio equal to 4:1. For the physical characterisation, besides the XRD measurement discussed before in figure 3.5, a SEM measurement has been performed. The SEM images are presented in figure 3.9 and give insight about the morphology of the samples. Similar to the 8:1 samples, the non-annealed composite shows a lamellae structure and MoO_3 microplates on the surface of it. For the annealed samples, less MoO_2 is visible on the surface of the V_2C and the lamellae structure is not visible anymore. This indicates that the interspaces of the V_2C are probably saturated, yet with less excess on top of the V_2C compared to the 8:1 composites.

In order to investigate the electrochemical processes, a CV measurement was performed. The CV data for all the samples is shown in figure 3.10. The scan rate is set to 0.05 mV s^{-1} . The OCV is 3.2 V. For the non-annealed sample, barely any electrochemical activity besides the V_2C is visible. In the first cycle only, several irreversible processes happen, up until around xxx V, where R_1 occurs. This peak is due to the intercalation into the V_2C . At 0.67 V, another peak attributed to the formation of an SEI is located, only on the first

cycle. The Peaks R_c and O_c are due to the carbon black added. O_1 is located at xxx V, but also is very faint. For the composite annealed at 400°C, the reoccurring peaks are more pronounced, while there are less irreversible processes at the beginning of the first cycle. Only R_x is the clearly visible peak at xxx V. R_1 is located at xxx V and as before, is due to intercalation into the V_2C . Interestingly, the peak attributed to the formation of a SEI is not directly visible in this CV measurement. Lastly, the composite annealed at 600°C is characterized. This time, a secondary peak is visible at 1.57 V/ 1.72 V. This peak could be attributed to the intercalation into the MoO_2 . The remaining peaks are similar to the other annealed composite.

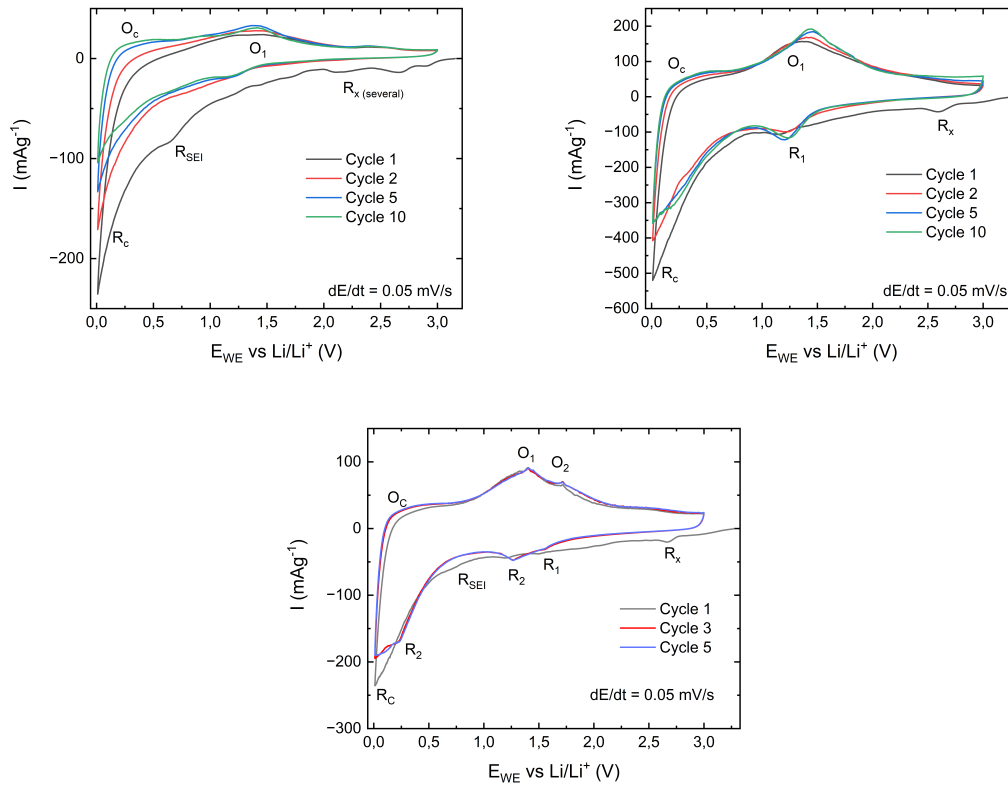


Figure 3.10: CV measurement of 4:1 MoO_3/V_2C in the 1st, 2nd, 5th and 10th cycle, recorded in the voltage range of 0.01 V - 3.00 V at a scan rate of 0.05 mV s⁻¹. Non-annealed left, 400°C right, 600°C bottom.

To determine the cycling stability and capacity of a cell, a GCPL measurement 3.11 has been performed using a current density of 100 mA g⁻¹ and a potential range from 0.01 V to 3.00 V. The initial lithiation capacity of the non-annealed sample is 1076.6 mAh g⁻¹ and 225.8 mAh g⁻¹ of the delithiation. The initial coulombic efficiency is 20.97%. This discrepancy is due to the formation of an SEI. Afterwards, the capacity is falling off to 285.1 mAh g⁻¹ at cycle 6. The non-annealed sample shows no further significant deviation from that value and stays stable for the rest of the measurement. The coulombic efficiency increases to 95.07% after the 6th cycle, which is consistent with the results of the pristine V_2C .

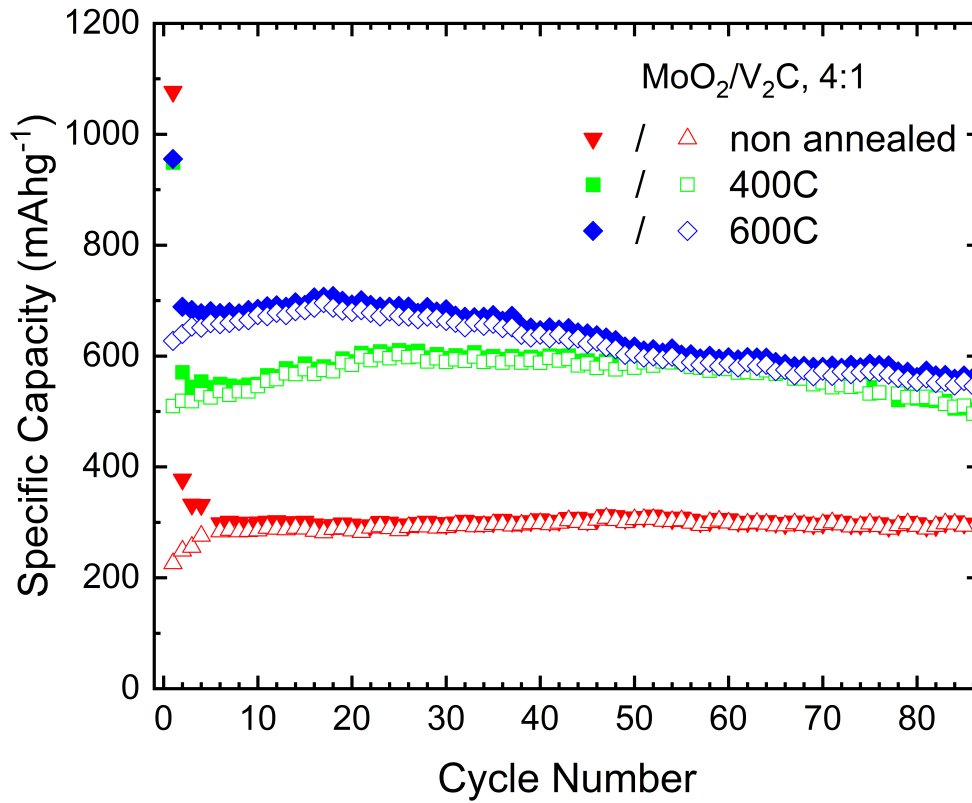


Figure 3.11: GCPL of 4:1 $\text{MoO}_2/\text{V}_2\text{C}$ recorded in the voltage range of 0.01 V - 3.00 V at a current density of 100 mA g^{-1} .

For the composite annealed at 400° , the initial capacity is 948.9 mAh g^{-1} for the lithation and 509.6 mAh g^{-1} for the delithiation. The coulombic efficiency is only 53.7%, due to the formation of an SEI. The capacity drops to 544.9 mAh g^{-1} after 8 cycles. The capacity increases in the following cycles up to a maximum of 603.8 mAh g^{-1} in cycle 24 and decreases to 485.2 mAh g^{-1} in cycle 92. Similarly, for the 600°C composite the initial capacity is 955.5 mAh g^{-1} for the lithation and 627.4 mAh g^{-1} for the delithiation. The coulombic efficiency is 65.7%, again due to the formation of an SEI. The reversible capacity increases up to 708.1 mAh g^{-1} in cycle 18 and decreases to 522.8 mAh g^{-1} in cycle 98. The degradation of the capacity could be attributed to the degradation of the host material during cycling, due to the effects of the conversion reactions, like e.g. large volume changes.

In this paragraph, the effects of annealing have been investigated on a more suitable composite mass ratio. The XRD measurement shows a superposition of MoO_3 and V_2C for the non-annealed composites and a superposition of MoO_2 and V_2C for the annealed composites. A higher crystallinity and a better integration of the MoO_2 into the V_2C can be deduced though the more pronounced peaks. In the SEM pictures, that hypothesis is supported, due to the smaller agglomeration of MoO_2 on top of the V_2C , compared to the 8:1 composites.

The CV measurements show that the conversion peaks seen in the 8:1 composites are less visible, meaning that the MXene is more functionalized. The 600°C composite still shows

some conversion activity.

The GCPL measurements show a stable cycling performance for the annealed samples, with an increase of capacity of up to 211.8% in the n th cycle for the 400°C composite and 248.4% in the n th cycle for the 600°C composite compared to the highest non-annealed capacity. This indicates that annealing significantly increases the specific capacity, at the cost of cycling stability, as the conversion reactions are more enabled, visible in the CV diagram.

Variation of the mass ratio

In the following, a short direct comparison between the two mass ratios will be done, with a conclusion about it afterwards.

As seen in figure 3.5, the 8:1 non-annealed composite seems to be more amorphous with only two peaks visible. In comparison, the 4:1 non-annealed composite shows some more pronounced peaks of MoO_3 and V_2C , showing that it is less amorphous. All the annealed samples show similar curves, with the 4:1 sample having clearer peaks than the 8:1 sample, thus being less amorphous again. The V_2C 4:1 sample seems to be less oversaturated than the 8:1 sample.

Comparing the SEM images shown in figures 3.6 and 3.9, we see some differences. Namely in the non-annealed samples, the h- MoO_3 microrods of the 8:1 sample are more visible compared to the microplates of the 4:1 sample. This is expected, due to the h- MoO_3 being more abundant. In both, the MXene structure is visible for the non-annealed sample. As stated before, the MXene structure becomes barely visible after the annealing, both for 400C and 600C. The 8:1 sample has significantly more leftover MoO_2 on the surface, which indicates that a saturation threshold has been passed and that there is not enough MXene to accommodate for all the MoO_2 .

Next up, comparing the CV measurements shown in figures 3.7 and 3.10 shows us that the 8:1 composites have a more pronounced phase transition of the MoO_2 rather than intercalation, as well as more pronounced peaks for the conversion reactions. The increase of the stability expected from the MXene is not as clearly seen as for the 4:1 sample, where the conversion reactions seem to be more suppressed.

Most importantly, the GCPL measurements 3.83.11 show us that the 4:1 composites, with a higher V_2C content, have a higher stability and similar capacity in comparison to the 8:1 composites, indicating that, for the mass ratio of 8:1, the added V_2C did not show the wanted effect of increasing the stability to its full potential. Increasing the amount of V_2C increased both stability and capacity. Overall, increasing the amount of MXene in a composite is a way to perhaps improve the further performance of a composite. Measurements with an even higher V_2C content might be of interest, as the 4:1 ratio still had some degradation over time, as well as excess MoO_2 on the surface.

3.3 WO_x/V₂C

As seen beforehand, annealing the composite is an effective way to significantly increase the reversible capacity of a given composite. investigate the effects of annealing on a different material, certain composites of WO₃ and V₂C will be characterized. The samples all have a given mass ratio of 8:1, only the annealing temperature is varied. In total, 4 composites are compared. The temperatures are: 200°C, 400°C, 600°C.

The XRD patterns are shown in figure 3.12. The non-annealed sample shows, similar to the MoO₃/V₂C-non-annealed composite, only a few peaks, three of them are very broad, only the peak at 8.6° is clearly visible. That one belongs to the V₂C, whilst the other peaks belong loosely to the WO₃. As for the XRD patterns of the annealed composites, they more closely resemble the WO₂ peaks, indicating that the WO₃ has reduced to WO₂ during the annealing process. Notable is the 23.6° peak, belonging to the V₂C. Thus, the V₂C seems to be saturated with the WO₂, and a higher annealing temperature increases the crystallinity of the sample.

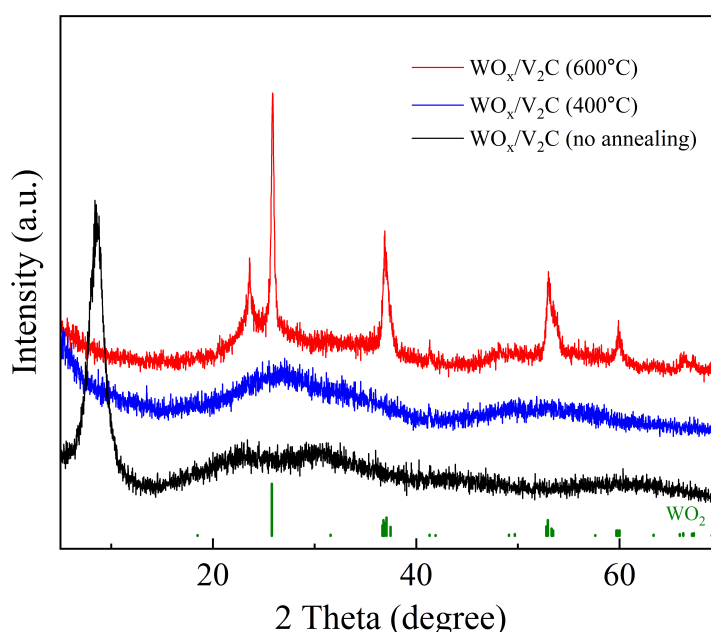


Figure 3.12: XRD patterns of different WO_x/V₂C composites, made by Peng Guo.

A SEM picture is shown in figure 3.13. For the non-annealed composite, the MXene structure is slightly visible, with a big agglomeration of loose WO₃.

To characterize the electrochemical process, a CV measurement 3.14 of the sample annealed at 600°C was made. The range was 0.1 V - 3.0 V with an OCV of 3.2V and a rate of 0.05 mV s⁻¹. In the first cycle, three irreversible process happen, at 2.80 V and 1.46 V two unknown processes happened, while at 0.64 V presumably, the formation of an SEI was taking place. The peak R₁ at around 0.95V was not clearly visible for the first cycle, due to some overlapping with other peaks and it's intensity decreased over

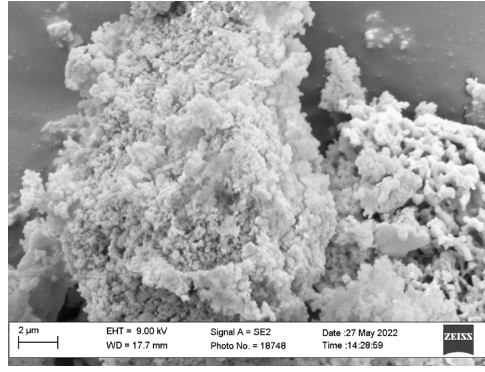


Figure 3.13: SEM picture of the non-annealed $\text{WO}_3/\text{V}_2\text{C}$ composite. Image made by Peng Guo.

time. This peak could attributed to the phase transition of the WO_2 , according to Fuije Chen et al. [30]. Furthermore, O_1 and O_2 , located at 1.09 V and 1.34 V, the first peak being attributed possibly to the deintercalation of the WO_2 and the second one due to the deintercalation of the V_2C , as it overlaps with the V_2C peak seen in figure 3.3. O_2 decreases significantly over time, which indicates a large degradation of the material over time. $\text{R}_\text{C}/\text{O}_\text{C}$ correspond to the de-/lithiation of the carbon black used in the composite. Not much overall information can be made from the measurement, more research needs to be put into the usage of the $\text{WO}_2/\text{V}_2\text{C}$ composite as an anode material.

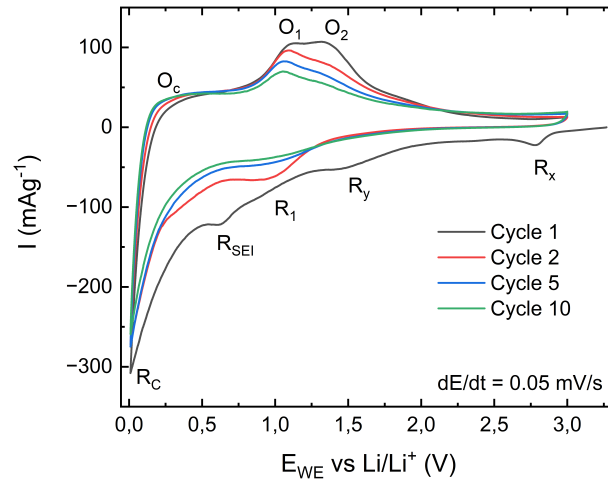


Figure 3.14: CV measurement of $\text{WO}_2/\text{V}_2\text{C}$, annealed at 400° , in the 1st, 2nd, 5th and 10th cycle, recorded in the voltage range of 0.01 V - 3.00 V at a scan rate of 0.05 mV s^{-1} .

Figure 3.15 shows the GCPL plot of the four composites. The current density is 100 mA g^{-1} , with a potential range of 0.1 V - 3.0 V. The non-annealed composite shows an initial lithiation capacity of 211.0 mAh g^{-1} and delithiation capacity of 55.5 mAh g^{-1} , with a coulombic efficiency of 26.3%, due to the SEI formation. The capacity drops to 63.2 mAh g^{-1} after 16 cycles. The composite annealed at 200°C shows an initial lithiation capacity of 173.7 mAh g^{-1} and delithiation capacity of 49.24 mAh g^{-1} , with a coulombic efficiency

of 28.3%, again because of the SEI formation. Similarly, the capacity drops to 48.6 mAh g⁻¹ after 10 cycles. The reversible capacity only sees a small increase over 100 cycles to 66.5 mAh g⁻¹ and 55.6 mAh g⁻¹ respectively. This small increase is probably due to the inter-layer spacing of the MXene widening over time as well as a better infiltration of the electrolyte, but those effects are marginal. The composite annealed at 400°C has an initial capacity of 699.3 mAh g⁻¹, dropping to 402.7 mAh g⁻¹ in cycle 5, increasing up to 422.1 mAh g⁻¹ in the 30th cycle and ultimately decreasing to 322.7 mAh g⁻¹ in cycle 100, caused by the conversion reaction. The decrease could further be due to the structural degradation of the host material over time. Furthermore, the composite annealed at 600°C shows a less steep decrease of capacity. The initial capacity is 554.9 mAh g⁻¹ first dropping in the second cycle, then increasing up until 457.5 mAh g⁻¹ in cycle 6 and dropping to 317.1 mAh g⁻¹ in cycle 100.

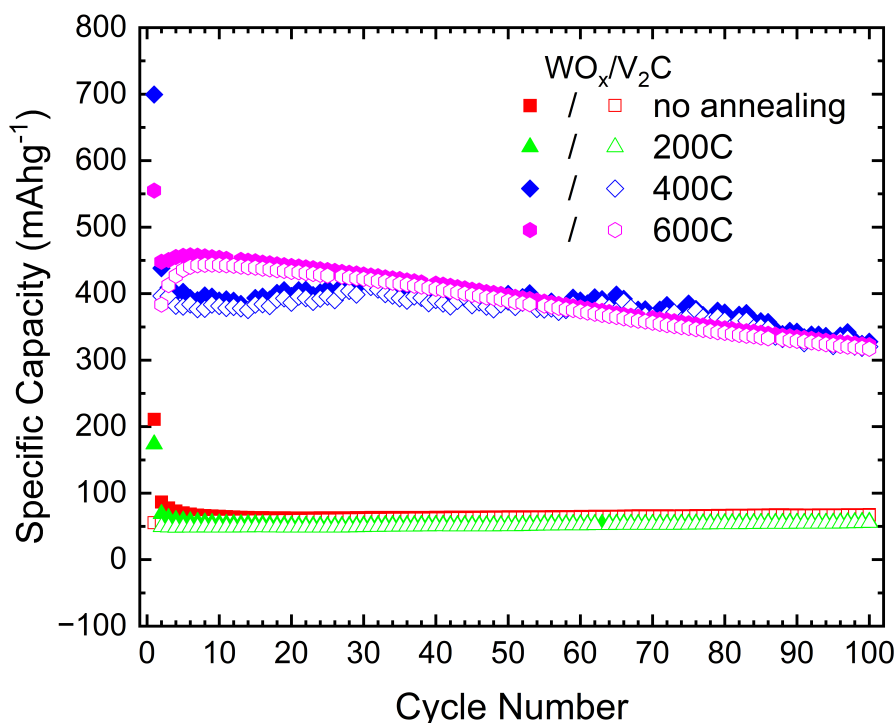


Figure 3.15: GCPL of WO_x/V₂C recorded in the voltage range of 0.01 V - 3.00 V at a current density of 100 mA g⁻¹.

In conclusion, similarly to the MoO_x/V₂C composite, annealing does significantly improve the battery performance of the WO_x/V₂C composite. Similarly, to the 8:1 MoO_x/V₂C composite, the MXene does not seem to completely satisfy the desired effect of stabilizing the composite during cycling. Perhaps trying a lower ratio of TMO to MXene, similar to the 4:1 composite before, could lead to better results. One can see that annealing at a lower temperature did little to no change on the performance of the composite. The increase in capacity during the annealing for this is remarkable and warrants further research.

4 Summary

In this work, two MXene-based nanocomposites, namely $\text{MoO}_x/\text{V}_2\text{C}$ and $\text{WO}_x/\text{V}_2\text{C}$, are prepared and investigated, regarding their cycling performance, intended to be used as an anode material used in LIBs. The influence of annealing and different mass ratios on the performance were investigated physically and electrochemically. All materials used were synthesized by Peng Guo.

In the first part, the pristine V_2C was characterized, to initially investigate its electrochemical properties and thus estimate its contribution in the composites. The XRD pattern shows that the synthesis has been successful, seeing that two new peaks emerge, in comparison to the precursor, whilst the main peaks diminish in intensity. The SEM pictures further show that the expected lamellae structure is visible. The cycling stability seems promising with a capacity of 182.2 mAh g^{-1} after 4 cycles and 213.2 mAh g^{-1} at 85 cycles, being in agreement with measurements done by Fanfan Liu et al. [27].

The main focus of this work is on the $\text{MoO}_x/\text{V}_2\text{C}$ composite and the effects of annealing on its physical and electrochemical properties. The XRD patterns show that during the annealing process, the MoO_3 used in the synthesis, got reduced to MoO_2 , changing the structure significantly. First measurements on composites with the mass ratio of 8:1 show that annealing has a positive influence on the electrochemical activity. GCPL measurements show an increase of the reversible capacity from 384.9 mAh g^{-1} up to 627.7 mAh g^{-1} for the 600°C composite. Yet, the stability during cycling is still not good. The MXene does not show the desired effect. To improve the stability, a higher ratio of V_2C to MoO_x was used to synthesize the composite, leading to both an improved capacity and stability. The SEM images show, that annealing changed the morphology of the composite, but also that the 8:1 composite has a large excess of MoO_x on the surface of the V_2C , while the 4:1 composite showed less excess on the surface. This composite shows a great potential as a novel anode material for LIBs. Further research is needed, finding out what the ideal annealing temperature is, as well as a more suitable mass ratio.

To further investigate the effect of annealing on TMO/MXene composites, a different TMO was investigated. Namely $\text{WO}_x/\text{V}_2\text{C}$ composites with a mass ratio of 8:1 were characterized. GCPL measurements show that annealing increases the capacity significantly, up to 457.5 mAh g^{-1} . It also revealed that there is a minimum temperature, as annealing at 200°C doesn't show any improvement. This material warrants further research, as it shows a great potential as a novel anode material for LIBs.

Overall, this work demonstrates that annealing a TMO/MXene composites leads to a sizeable improvement of the performance. Further research in this field could yield a big contribution towards the goal of making TMO/MXene composites a suitable anode material for LIBs.

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Erklärung

Ich versichere, dass ich diese Arbeit selbstständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt habe.

Heidelberg, den 11.10.2022,

A handwritten signature in black ink, appearing to read 'Blin'.