Abnormal Phenomena of Multi-Way Sodium Storage in Selenide Electrode

Anna Plewa,* Andrzej Kulka, Emil Hanc,* Jianguo Sun, Mikołaj Nowak, Katarzyna Redel, Li Lu, and Janina Molenda

Transition-metal chalcogenides have gained special attention as potential anodes for Na-ion batteries due to their high capacities to originate from complex charge storage mechanisms. Although the sodium storage process in chalcogenides is still unclear, it is common to assume that it can occur via one of the following routes: intercalation, conversion, or alloying. In this paper, an anomalous multi-way mechanism in MoSe$_2$ electrode, including all three of the above scenarios, is reported. The intercyclic product of the discharge/charge process is a mixture of Se, Mo, and 1T-structured Na$_x$MoSe$_2$. An unexpected phenomena of Se precipitation leads to the additional alloying charge/charge process is a mixture of Se, Mo, and 1T-structured Na$_x$MoSe$_2$. An unexpected phenomena of Se precipitation leads to the additional alloying reaction, which is exclusive among all chalcogenides, and runs together with conversion and intercalation reactions in the same cycle. This new concept of sodium storage process includes two models, previously seemed to be mutually exclusive. Despite of complex electrode mechanisms, MoSe$_2$ retains high capacity and coulombic efficiency even after 50 cycles.

1. Introduction

The rechargeable batteries are essential for energy storage systems and with growing energy demand, the need for such batteries constantly increases. Although lithium-ion battery (LIB) is a comparatively mature and widely used technology, considering the resources availability versus massive utilization of Li, economic and geopolitical issues, the wide applicability of LIBs technology may become challenging in near future. Therefore, alternative post-lithium-ion technologies including Na-, K-, Mg-ion types batteries are intensively developed these days. Due to the abundance and even distribution of sodium resources, the sodium-ion batteries (SIBs) are emerging as a potential substitute for LIBs.

Although lot of research was performed for promising cathodes materials, for example, Na$_{0.6}$Mn$_{0.3}$Fe$_0.5$O$_2$[1], NaFe$_0.1$Co$_0.9$O$_2$[2], Na$_2$MnO$_2$[3], Na$_{0.6}$Mn$_{0.5}$FeO$_2$[4], Na$_2$V$_2$(PO$_4$)$_3$[5] poly-anion compounds such as Na$_2$Fe$_2$(SO$_4$)$_3$[6], Na$_3$V$_2$PO$_4$[7], Na$_{11.12}$Mn$_{2.44}$(P$_2$O$_7$)$_3$/C[8] as well as Prussian blue analogues[9,10], the developing of anode materials for SIBs remains challenging. Since graphite as a benchmark anode for LIBs is not applicable for SIBs[11] the major milestone toward SIBs commercialization is to find suitable anode material. Generally, the anode materials may be classified according to three distinct charge storage mechanisms: alloying, conversion, and intercalation. Among them, Na$^+$ storage occurring via intercalation is the most common process which covers Ti-based (e.g., Na$_{0.6}$Li$_{0.22}$Ti$_{0.78}$O$_2$[11], Na$_2$Ti$_3$O$_7$[12]) and carbonaceous anodes (e.g., hard carbon, carbon nanotubes[13]). These materials exhibit good reversibility and small volume changes. Nonetheless, the reversible intercalation of Na$^+$ is mostly limited by the deformations that the crystal structure can withstand and the limited redox activity of the transition metals[14].

This type of anode has intrinsic limitations in terms of capacity, thus further increase of the energy density can be expected using different storage mechanisms. The extremely high values can be achieved from alloying reactions between Na and Sn or P to form, for example, Na$_{15}$Sn$_4$ or Na$_3$P. However, the practical utilization of these reactions has been severely limited by the huge volume changes (even 400%) associated with the (de)sodiation process, which results in large strains generation within the particles, subsequently leading to capacity loss upon cycling.[15]

The discovery of the third type of Na storage reaction referred as conversion mechanism brought a compromise between
high capacity and small volume changes. The key to the reversibility of the conversion reactions lies in the formation of metal nanoparticles with large interfacial surface, embedded in sodium compounds. Such metal nanoparticles are very prone to decompose the structure of sodium compounds when a reverse polarization is applied. Nevertheless, strong structural reorganization induces volume changes, higher than in the case of intercalation, which can lead to unsatisfactory cycling performance.[16] Conversion-based anodes mainly include the compounds of transition metals with oxygen, nitrogen, phosphorous, sulfur, or selenium. Among them, transition-metal dichalcogenides (TMDs) gained special popularity since their sodium storage mechanism is a unique combination of alloying, conversion, and intercalation reactions.[14,17] One of the very intriguing representatives of TMDs group is MoSe2 which recently has gained increased research attention. MoSe2 crystallizes in a sandwich structure (inorganic 2D graphite-like structure) in which the Se=Mo-Se layers with covalently bonded in-plane atoms are held together by weak van der Waals forces. The large interlayer spacing of MoSe2 (0.65 nm), significantly larger than graphite (0.34 nm), favors freely Na insertion/removal and the theoretical capacity of this material can reach even 422 mAh g$^{-1}$ (calculated based on the conversion-based reaction).[17,18]

Up to date, the research was mainly focused on the development of the most suitable synthesis procedure of MoSe2 with enhanced electrochemical performance. Shu Tian synthesized MoSe2@C nanofibers by electrospinning, which delivered a specific capacity of 390 mAh g$^{-1}$ at 1 A g$^{-1}$.[19] Amlan Roy et al. prepared MoSe2 embedded in N,P-doped graphene sheets by a solvothermal route which showed capacity of 337 mAh g$^{-1}$ at 0.1 A g$^{-1}$ after 100 cycles.[20] Furong Qin et al. presented mesoporous MoSe2/C composite obtained by nano-casting technique, which showed capacity of 379 mAh g$^{-1}$ at current density of 200 mA g$^{-1}$.[21] However, the engineering of the appropriate electrochemical properties of MoSe2 requires in-depth understanding of processes occurring during cycling. Thus, aiming to reveal the detailed charge storage mechanism Wang et al.[22] using ex situ XRD measurement proposed that MoSe2 after first discharge converts to the mixture of Na2Se and Mo phases, according to the equation MoSe2 + 4Na++4e$^- = Mo + 2Na2Se$ reaction. Subsequently, during the 1st charge MoSe2 is supposed to be restored from Mo and Na2Se phases upon Na removal. Contrary, Roy et al.[20] as well as Xie with co-workers[23] using ex situ XRD, XPS, TEM, and Raman methods found that during the first charging process, the electrochemical reactions involve rather oxidation of Se$^{2-}$ (from Na2Se) to Se0. That imputes, Se0 instead of MoSe2 was restored after the first cycle and electrochemical processes in subsequent cycles were based on the alloying reaction between Se and Na$^+$. Though some work has been done so far, the exact mechanism of the sodium storage mechanism in MoSe2 remains elusive, with a crucial puzzle concerning the charge products after the initial cycle process. Mainly due to the inability to detect the signal of metallic Mo by ex situ techniques, as a result of the strong reactivity of Mo nanoparticles with air, its role was not clarified yet.

Since the ex situ approach turned out to be an insufficient tool in in-depth investigation of the (de)sodiation mechanism of MoSe2 electrode, within this work we applied comprehensive approach of using combined operando XRD and ex situ XANES with deep penetration mode to avoid the effect of surface reactivity. By means of the operando XRD analysis we identified phases of initial cycle and described in detail Na$^+$ intercalation process including lattice parameters evolution of 2H and 1T phases. Chemical analysis by XPS enabled us to characterize products of the initial cycle. By means of XANES analysis, we observed evolution of selenium oxidation state and identified variety in the local coordination chemistry of Se and Na atoms during 1st and 2nd cycles, which allowed us to define points of system transformation. Obtained information of structural evolution was combined with in situ EIS study to describe the kinetic of Na$^+$ (de)insertion reactions by determination of charge transfer resistance and diffusion coefficient progress.

Consequently, we present the new theory of sodium storage in selenides, which combines two models, up to day seemed to be mutually exclusive. It is based on abnormal phenomena of selenium precipitation, which is exclusive among all chalcogenides and contributes to the selenide systems’ high capacity. We propose (de)sodiation process in MoSe2 as a model for whole selenides family.

2. Results
2.1. Structure and Morphology of MoSe2

The synthesis of MoSe2 by the hydrothermal route with subsequent high-temperature annealing is illustrated in Figure S1a, Supporting Information, and specified in the Experimental Section. In contrast to the typical procedure,[14,17] hydrazine hydrate and 20% ethylenediamine water solution were used as solvents for selenium powder and Na2MoO4, respectively. Hydrazine acts as a reducing agent during molybdenum reduction from (+VI) to (+IV). Since bulk crystals of TMDs are expanded volumetrically by reacting with hydrazine under hydrothermal conditions, the hydrazine also plays exfoliation role.[18] The ethylenediamine was chosen mainly as a morphology controlling reagent, however it also acts as an intercalating reagent expanding the interspacing of MoSe2 layers. The hydrothermal reaction was performed in the mixed solution at 160 °C for 20 h. In order to remove the organic residue, the products were treated in Ar/H2 (95%:5%) at 600 °C for 2 h. The temperature was chosen based on previous thermogravimetric studies according to which there is no weight loss above 500–550 °C.[22,25–27] Figure S1b, Supporting Information, depicts the X-ray diffraction pattern of the as-synthesized product. All peaks can be indexed to the hexagonal crystal structure with P63/mmc space group of MoSe2 (namely 2H-MoSe2). In general, three diffraction peaks related to (002), (100), and (110) set of diffraction planes are characteristic for hexagonal 2H-TMDs. Among them, the (002) peak corresponds to the reflection from a set of atomic planes parallel to the basal plane of 2H-TMDs and is the most intense one for the bulk crystalline form. The fade out of (002) reflection is fingerprint for few-layer or monolayer nanosheets form of 2H-TMDs.[28] Moreover, when the dimensions of the materials were reduced down to monolayer nanosheets, the XRD patterns do not show (110) reflection but (100) would still be observable.[18] Thus, analysis of the mutual intensity of (002), (100), and (110) can provide detailed information concerning the dimensions of the 2H-MoSe2 materials. In discussed X-ray diffraction pattern of as-synthesized...
2H-MoSe\(_2\) (Figure S1b, Supporting Information) the intensity of (002) reflection is slightly weaker than in-plane (100), however the (110) reflection is still observed what indicates the few-layer nanosheets form of 2H-MoSe\(_2\). The refined values of the lattice parameters of synthesized MoSe\(_2\) are equal to \(a = b = 3.27 \, \text{Å}, \quad c = 13.27 \, \text{Å}, \quad V = 122.65 \, \text{Å}^3\). Interestingly we found that the lattice parameter \(c\) is increased significantly compared to reported in PDF card nr 04-004-8782 (\(c = 12.93 \, \text{Å}\)) indicating expanded MoSe\(_2\) structure. It can be a result of the usage of structure-expanding additions during synthesis. Whereas \(a, b\) parameters remain in good agreement with referenced card (\(a = b = 3.28 \, \text{Å}\)). Refinement fault observed mainly in intensity of (110) reflection could be probably related to Mo–Se arrangement layers.

The characteristic 2H-MoSe\(_2\) Raman peaks associated with \(A_{2g}\) and \(E_{1g}\) modes are identified at 238.1 and 284.2 cm\(^{-1}\), respectively (Figure S1c, Supporting Information). \(E_{2g}\) involves an in-plane vibration of the sublattice formed by Mo atoms against the sublattices formed by Se. Whereas \(A_{1g}\) corresponds to out-of-plane vibrations of the upper and lower sublattices of Se atoms against each other.\(^{[29]}\) \(A_{1g}\) mode of 2H-MoSe\(_2\) shows a redshift compared to the MoSe\(_2\) bulk material (\(A_{1g} = 240.6 \, \text{cm}^{-1}\)) indicating few-layered MoSe\(_2\) nanosheets form and confirms enlarged spacing between interlayers.\(^{[27]}\) The same progression of in-plane mode (\(E_{2g} = 283 \, \text{cm}^{-1}\) for bulk material\(^{[20]}\) may be attributed to long-range Coulombic interlayer interactions.\(^{[21]}\) Moreover, the Raman spectrum analysis shows that the \(A_{1g}/E_{2g}\) intensity ratio of the bare MoSe\(_2\) reported previously and our MoSe\(_2\) is reduced from 1.99 to 0.75 indicating that the number of layers is reduced.\(^{[32]}\)

According to scanning electron microscopic (SEM) microphotographs (Figure S1d, Supporting Information), it can be seen that MoSe\(_2\) particles were agglomerated forming clusters due to high surface energy and Van der Waals attraction, consequently leading to spheres of diameter in ≈500–700 nm range. Their shape can be described as snowballs built of nanosized spheres. A similar effect of spherical MoSe\(_2\) structure was also observed by Jie Li et al.\(^{[31]}\) by using the hydrothermal method. Energy dispersive spectroscopy analysis (EDS) presents that Mo:Se ratio is almost equal to 1:2, which confirms the as-synthesized MoSe\(_2\) as the final product. Result of EDS analysis is presented in Figure S2, Supporting Information.

### 2.2. Electrochemical Characterization for Initial Cycles

Aiming to get in-depth understanding of the electrochemical properties of the investigated MoSe\(_2\), the as-synthesized material was thoroughly characterized as an anode in Na-ion type cells. Unlike previous studies where NaClO\(_4\) in PC, EC:DMC, or EC:DEC were usually used as an electrolyte\(^{[34–36]}\), we chose NaPF\(_6\) 1 M solution in diglyme solvent. We found that in case of 1 M solution NaPF\(_6\) in EC:DEC an electrolyte, the MoSe\(_2\) shows a significant capacity loss from 520 to 200 mAh g\(^{-1}\) after 10 cycles (Figure S3, Supporting Information), while Na[Na\(_x\)]MoSe\(_2\) with NaPF\(_6\) in diglyme is characterized by much better cycling performance. Moreover, it was found that the NaPF\(_6\) 1 M solution in diglyme acting as a electrolyte reduces irreversibility of the reactions during the first discharge, improves Coulombic efficiency and capacity retention in subsequent cycles.\(^{[35]}\) Figure 1a shows the galvanostatic charge/discharge profiles for the 1st, 2nd, and 10th cycle at a 0.05 A g\(^{-1}\) current density. We found that the initial capacity of investigated anode is 510 mAh g\(^{-1}\), which is considerably higher than the theoretical one (422 mAh g\(^{-1}\)). We suspect that this high value was not only due to the decomposition of the electrolyte and the formation of the solid electrolyte interface (SEI) layer, but could be also associated with some other mechanisms occurring upon sodiation process. After the initial capacity loss, 360 and 355 mAh g\(^{-1}\) is achieved in 2nd and 10th cycle, respectively. Similar results for pristine MoSe\(_2\) were observed by Wang et al.\(^{[22,38]}\) who reported discharge capacity decrease from 513 to ≈360 mAh g\(^{-1}\) after 10 cycles at 0.1 C current density (0.1 C equals 0.042 A g\(^{-1}\)).

Until now, two stages of Na\(^+\) insertion into MoSe\(_2\) during 1st discharge was proposed similar to MoS\(_2\).\(^{[39]}\) Those considerations assume the intercalation of sodium ions to form Na\(_x\)MoSe\(_2\), and subsequently the conversion reaction to Mo metal and Na\(_2\)Se.\(^{[40]}\) However, when we analyze the voltage profiles and CV curves (Figure 1), during the first discharge we found not two but three stages of sodiation, at ≈0.4, 0.7, and 1.2 V, better seen on the dQ/dV curve (Figure 1c). We suspect that taking well-known MoS\(_2\) as a model for 1st discharge of whole chalcogenides family was the erroneous approach.

We also found the difference between 1st discharge-charge profiles and reduction-oxidation curves indicating most probably the different processes of sodiation and desodiation in MoSe\(_2\) electrode during 1st cycle. Interestingly, the voltage and CV profiles of 1st and subsequent charge curves are similar, while the 1st discharge curve differs considerably from 2nd and 10th discharge voltage dependences. It suggests that the electrochemically active phases which are formed in the electrode after 1st discharge are responsible for charge storage in subsequent cycles. It may be suspected that indeed the electrode undergoes irreversible reaction during 1st discharge, however the reactions observed in further cycles are highly reversible.

### 2.3. Structure Evolution of Selenide Electrode

#### 2.3.1. Operando XRD evaluation

Operando XRD patterns for MoSe\(_2\) electrode were collected during the first discharge/charge cycle and are shown in Figure 2a. At the beginning of the process, the diffraction peaks for 2\(\theta\) = 13.8\(^{\circ}\), 31.8\(^{\circ}\), and 56\(^{\circ}\) can be assigned to 2H-MoSe\(_2\) phase. During the first stage of intercalation, in voltage range 2.5–0.5 V, we observed the transformation from 2H-MoSe\(_2\) to 1T-Na\(_x\)MoSe\(_2\) phase, confirmed by the evolution of the unit cell parameters obtained from refinement of the XRD patterns. Since there are no crystallographic data available of 1T-MoSe\(_2\) we use the simulated data from DFT calculation as a reference for refinement (Table S1, Supporting Information). While the Na content increases (Figure 2b), the \(a\) lattice parameter enlarges, which could be related to the changes of Mo–Mo distance during the reduction of Mo\(^{4+}\) (\(r = 0.65 \, \text{Å}\)) to slightly greater Mo\(^{3+}\) (\(r = 0.69 \, \text{Å}\)).\(^{[40]}\) Moreover, the increase in \(a\) parameter is bigger in the case of 1T-Na\(_x\)MoSe\(_2\) than for 2H form. The decrease in \(c\) lattice parameter upon sodium insertion corresponds to the weakening of anions repulsion due to the increase of the screening effect induced by presence of Na.
ions. Further, below 0.5 V, we found that the diffraction peaks originating from 1T-Na$_x$MoSe$_2$ vanish, suggesting the end of the intercalation mechanism region. Meanwhile, peaks at \( \approx 38.9^\circ \) and 54° appear confirming the formation of metallic Mo, which can be understood as an onset of conversion reaction. The height of these peaks increases till the end of discharging meaning the rise of Mo content, in turn suggesting continue progress of this process. Simultaneously, Na$_2$Se is formed, however the detailed observation of the evolution of its diffraction peaks is hindered since the Na$_2$Se peak overlaps with the one from Mo. Unexpectedly, when the voltage reaches \( \approx 0.8 \) V, new peak at 31.5° appears, slowly increasing as the sodiation proceeds and getting the maximum of its intensity at about half of the discharge process. Later it gradually decreases till the end of the discharging process. Since it is much sharper and higher than the peaks for MoSe$_2$ structure, it cannot be ascribed to this phase. Surprisingly, after detailed investigation, we found this peak to be attributed to Se (PDF card nr 04-021-6791), characterized by hexagonal symmetry with P3$_1$21 space group. Selenium in such form was previously reported as electrode for Na-Se and Li-Se batteries.[42] Se precipitation during the 1st discharge was not observed previously for chalcogenides family, suggesting that charge storage in selenides is more complex than in other members.

During the charging process, Mo is still observed up to upper limit voltage, while the intensity of the Se peaks increases in the first half of charging and then remains constant till the end of desodiation. We found the formation of the broad reflection peak at 56°, most probably corresponding to MoSe$_2$ phase. The peak’s intensity increases, and at the end of the charge process when abrupt change in voltage shape is observed, it becomes slightly more pronounced. The formed peak is different than observed at the beginning of measurement, which suggests the formation of MoSe$_2$ in different form than pristine material. However, it is difficult to determine whether this is a pure MoSe$_2$ or partially sodiated phase based on the only XRD measurement.

### 2.3.2. Chemical analysis by XPS

Further investigation of reactions taking place during 1st cycle was carried out by means of X-ray photoelectron spectroscopy (XPS) analysis (Figure 3). Three samples were chosen (marked in Figure 2a: before cycling—A1, after the first cycle (discharging-charging)—A8 and at specific point at charge curve (1.7 V) corresponding to oxidation peak in CV scan—sample A6 (Figure 1d). Mo 3d spectrum of the A1 sample shows two peaks at 229.2 and 233.8 eV, which can be assigned to Mo 4$^{\text{+}}$ oxidation state and confirming MoSe$_2$ as a pristine sample. For the other two samples, the molybdenum was found in two oxidation states and thus Mo 3d spectra were fitted with two doublet structures (d$_{3/2}$ - d$_{1/2}$ doublet separation equals 3.13 eV) with the first 3d$_{3/2}$ line (orange) centered at 229.0 eV which indicate Mo$^{4+}$ oxidation state, second 3d$_{3/2}$ line (purple) centered at 233.1 eV originates from the presence of Mo$^{6+}$ state.[43,44] Noteworthy, during the charging process at voltage 1.7 V intensive signals from Mo$^{6+}$ are detected. As mentioned before the existence of metallic Mo in this region is proved by operando XRD, since Mo in this form is very active and can be easily oxidized during disassembling of the coin cell. Therefore, we suggest that molybdenum is present rather in form of Mo$^{6+}$, as a result of oxidation by atmospheric air, than metallic Mo$^{0}$. This effect was observed in previous research for MoS$_2$ and most probably confirms the existence of metallic Mo.
After a full charge when the voltage reaches 3 V, signals from both forms of Mo are visible, however Mo$^{6+}$ decreases contrary to Mo$^{4+}$. Therefore, the products of 1st cycle (A8) include metallic Mo and MoSe$_2$, which is in good agreement with operando XRD. Moreover, between XPS spectra for pristine sample and sample after 1st discharge-charge process we observed the shift of the Mo$^{4+}$ line toward lower binding energy, indicating that after 1st cycle the MoSe$_2$ comes back to rather IT structure than 2H as in the pristine one. Further, the Se 3d spectra for the pristine sample was fitted with one doublet structure ($d_{5/2} - d_{3/2}$ doublet separation equals 0.9 eV) with the main 3d$_{5/2}$ line positioned at 54.5 eV which indicate the presence of MoSe$_2$ compound, suggesting an oxidation state of Se$^{2-}$. After charging at voltage, a 1.7 V ratio between $d_{5/2}$:$d_{3/2}$ goes to 1 and after 1st cycle, this ratio decreases similar to the pristine one, whereas the FWHM value increases compared to pristine one. The shift toward lower energy confirms obtaining IT structure after 1st cycle.

As expected, sodium was not detected in the A1 sample. In the A6 and A8 sodium was found to exist in the two different states: the first peak centered at 1072.3 eV (Na11s) and the second spectral line positioned at 1074.4 eV (Na 21s). Interestingly, the sodium is observed at XPS spectra for A8 sample (after charge), most probably meaning that sodium remains in the product of 1st cycle, in the form of partially sodiated Na$_x$MoSe$_2$ or product of side reactions, for example, SEI formation.

2.3.3. XANES Analysis at Se L-Edge and Na K-Edge during First and Second Cycles

X-ray absorption spectroscopy (XAS) measurement was conducted in selected points chosen taking into account the characteristic points at voltage profiles and peaks on CV curves. Points are shown in Figure S4, Supporting Information.
XANES spectra of the sodium K-edge and selenium L\textsubscript{2}- and L\textsubscript{3}- edge were collected in total fluorescence yield (TFY), since FY mode gives information from the bulk of material unlike the surface-sensitive total electron yield (TEY) mode. Figure 4 shows the evolution of Se L-edge during first discharging/charging cycle. Data for A1–A4 points were collected during the 1st discharge (Figure 4a). The Se L\textsubscript{2} pre-peak position moves toward higher energy from sample A1 to A2, indicating oxidation of selenium. Then for A3 and A4 come back toward lower energy, indicating Se reduction. The oxidation and reduction process of selenium during charging was postulated in previous sections and XANES results seem to confirm it. Additionally, significant change of the shape of L\textsubscript{3}-edge between A1/A2 and A3/A4 samples is observed. It is related to an alternation in the local coordination chemistry of Se atoms, induced by phase transitions from Na\textsubscript{x}MoSe\textsubscript{2} to Se and Na\textsubscript{2}Se. The changes of oxidation state and first coordination sphere are also seen in Se L\textsubscript{2}-edge. During charging, the pre-peak of Se L\textsubscript{3}-edge moves toward higher energy for sample A5, A6, A7 (Figure 4b), thereby confirming the oxidation of Se\textsuperscript{2-} to Se\textsuperscript{0}. For A8 pre-peak goes back toward lower energy indicating a partial reduction of Se and can be connected with a partial reformation of MoSe\textsubscript{2}. Importantly, the L-edge for sample A2 and A8 are quite similar suggesting similar valency and crystallographic environment of selenium which is in good agreement with previous speculations, suggesting reconstruction of MoSe\textsubscript{2}-type phase. XANES spectra of Se L-edge for the second cycle are presented in Figure S5, Supporting Information. The spectrum for B9 and B10 samples exhibit similar characteristics, suggesting that reversible processes occur during discharging-charging after the initial cycle. Spectra at the end of 1st and 2nd cycle are the same indicating that the same product is obtained after the initial and second cycle. Moreover, the same position of L-edge for A6 and B10 samples indicates the same oxidation state and coordination of Se during 1st and 2nd charging at voltage \approx 1.7 V.

XANES spectra for Na K-edge are shown in Figure 5. Easily observed difference between edge of A2 and A3/A4 samples suggests the different atomic first coordination sphere. While the cell voltage goes from 0.7 V (A2) through 0.5 V (A3) to 0.05 V (A4) the sodium XANES spectral features at 1078 eV rise in intensity, what is accompanied by the decrease of the intensity of the feature at 1083 eV (Figure 5a). Edge position remains at the same energy, indicating no change of valence state. A3 point corresponds to the main reduction peak on CV curve at \approx 0.4 V. The recorded spectrum for A3 and A4 are compared with the references simulated spectrum for Na\textsubscript{2}Se in Figure 5b. A similar characteristic suggests the appearance of Na\textsubscript{2}Se at the end of the discharge process. In Figure 5c we observed a significant difference between shape of the spectra for samples A5/ A6 and A7/A8 what is assigned to processes taking place before and after main oxidation peak on CV curve during 1st charging. Looking at the evolution of the spectra from A5 to A8 sample,
we found that the pre-peak and features at 1077 and 1085 eV decrease during the desodiation process and the second peak (at ~1085 eV) splits into two. Significant differences (A5/A6 contrary to A7/A8) are visible in shape on XANES spectrum after the absorption edge suggesting an essential modification of further sodium coordination spheres, most probably due to the partial transformation of Na₂Se to NaₓMoSe₂ phase. Figure S6, Supporting Information, presents Na K-edged for second cycle in selected points. Similar to the conclusion from XANES Se L-edge analysis samples B9 and B10 are characterized by the same XANES spectrum suggesting reversible process of oxidation and reduction. During charging (B10 and B11) there is a change in the intensity ratio of features at 1080 and 1088 eV. Taking into account the similar shape of spectrum for A6 and B10 points it can be assumed that similar reaction takes place during 1st and 2nd charging.

2.4. Kinetics of Sodium (De)Insertion

In situ electrochemical impedance spectroscopy (EIS) was carried out to analyze the reaction dynamics of MoSe₂ during the initial cycle (Figure S7, Supporting Information). During the 1st discharge at voltage 0.7 V instant growth of diffusion coefficient (Dₙa) for two orders of magnitude is observed. At the same point of discharge precipitation of metallic Mo and Se appear according to operando XRD analysis. It confirms that Se and Mo are appearing before intercalation process is ending. The chemical diffusion coefficient remains constant until ~0.4 V and then starts decreasing till the end of discharge. In the same voltage range we observed on the operando XRD patterns that the diffraction peaks from Se decrease in favor of Na₂Se. During desodiation Dₙa coefficient decreases till voltage reach 1.7 V. That point can be linked to the oxidation peak on CV curve (Figure 1d) related to the reconstruction of MoSe₂ phase and most likely slow diminishing of the metallic Mo phase.

The cycling performance of the MoSe₂ half-cell was evaluated by cyclic galvanostatic charge/discharge measurement with 0.05 A g⁻¹ current density for 50 cycles (Figure 6a). The initial discharge capacity is 513 mAh g⁻¹, which falls to 390 mAh g⁻¹ in the 2nd cycle and gradually decreases in subsequent cycles. Interestingly, the charge capacity increases in the first 5 cycles, and then rapidly decreases in the next eight ones and stabilizes in the following cycles. Such a behavior most probably originates from the intense structural reorganization during the first cycles discussed in the previous sections.
After 15th cycle there is no obvious decay of the charge and discharge capacity. It can be concluded that few initial cycles are needed to complete structural transformations and establish equilibrium between electroactive phases. From the 15th cycle on, the Na\textsuperscript{+}/Na\textsuperscript{+}\textsubscript{MoSe\textsubscript{2}} delivers a capacity of 320 mA h g\textsuperscript{−1} and keeps nearly 100% Coulombic efficiency. During the rate capability test the electrode was cycled under the current load ranges from 0.05 to 0.2 A g\textsuperscript{−1} and then returned to 0.05 A g\textsuperscript{−1}. As shown in Figure 6b the MoSe\textsubscript{2} electrode exhibits final discharge capacities of 350, 270, 200 mA h g\textsuperscript{−1} at current densities of 0.05, 0.1, 0.2 A g\textsuperscript{−1}, respectively. After return to current density 0.05 A g\textsuperscript{−1} the discharge capacity got back to 350 mA h g\textsuperscript{−1} indicating superior rate capability with low capacity fade.

The CV curves of different scan rates are shown in Figure 6c. As indicated in the previous section, the first scan at a 0.1 mV s\textsuperscript{−1} scan rate is different from the further ones. Since second cycle there are three corresponding reduction and oxidation peaks (I-II-III and I’-II’-III’) indicating three stages of Na storages mechanism. Noteworthy, potential shifts between cathodic and anodic processes increase from I to III reactions. When the scan rate increases the ratio of peaks changes indicating different kinetics of particular reactions taking place during cell cycling.

3. Multi-Way Sodium Storage

The schematic representation of sodium (de)insertion mechanism is shown in Figure 7. The XRD, Raman, and XPS measurements confirmed that the starting MoSe\textsubscript{2} material exhibit hexagonal 2H phase. We found by the operando XRD analysis that the first stage of sodiation, till the voltage reaches \approx 0.8 V, proceeds via intercalation of Na ions into 2H-MoSe\textsubscript{2} structure. Below the 0.8 V the 2H phase is no longer energetically favorable and during constant Na ions intercalation gradually rearranges to 1T-Na\textsubscript{x}MoSe\textsubscript{2} structure. Interestingly, contrary to ordinary intercalation/conversion reactions, we found that Se\textsuperscript{0} and Mo\textsuperscript{0} precipitation simultaneously proceed to Na ions intercalation into Na-rich Na\textsubscript{x}MoSe\textsubscript{2}, which is seen in operando XRD patterns as an appearance of reflexes at 31.5° and 38.3° for Se and Mo, respectively. The oxidation of Se\textsuperscript{2−} toward Se\textsuperscript{0} during sodiation is also confirmed in XANES spectra by shifting toward higher energy of the pre-peaks of L\textsubscript{2} and L\textsubscript{3} edges. While the sodium insertion process continues, below 0.5 V the Na\textsubscript{x}MoSe\textsubscript{2} structure collapses implying end of intercalation process. It can be linked with the main reduction peak on the CV curve. Consequently, from this point until the end of 1st discharge the conversion reaction of Na\textsubscript{x}MoSe\textsubscript{2} to...
Mo and Na$_2$Se phases takes place. However, in the electrode already exists Se$_0$ originating from prior precipitation reaction, simultaneously with the conversion reaction we observed the additional alloying process between Se$^0$ and Na$^+$ leading to the formation of extra Na$_2$Se at the end of discharge. Therefore, the final product of 1st discharge includes metallic Mo arose from conversion reaction and Na$_2$Se originating from two parallel reactions: conversion and alloying. During the charging process in the early stage of desodiation, the Na$_2$Se disintegrates into Se$^0$ and Na$^+$ ions, initializing the dealloying process. Probably this reaction runs simultaneously to another one, where Na$_2$Se takes part in reconversion with Mo. Subsequently, at 1.7 V the amount of Se$^0$ in this system reaches the maximum and from this point begins to react with Mo$^0$ what consequently leads to the reconstruction of MoSe$_2$-type phase. This reaction can be linked with the main oxidation peak at.

![Figure 6](image-url)  
**Figure 6.** a) The cycling properties of Na|MoSe$_2$ cell. b) Specific capacities as a function of current rates and cycle number. c) The cyclic voltammograms as a function of scanning rate $\nu$.

![Figure 7](image-url)  
**Figure 7.** Schematic representation of sodium (de)insertion mechanisms taking place during discharge/charge cycles of Na|MoSe$_2$ cell along with its voltage characteristics for 1st and 2nd discharge/charge cycle.
1.7 V on CV curve. This effect is seen by partial reduction of Se0 showed by XANES analysis, the appearance of Mo4+ peaks on XPS spectrum and MoSe2 reflections on XRD patterns. Based on XPS analysis we found that selenide is reformatted into the IT-types phase, while the residual sodium is still observed in the final product of desodiation, most likely in the form of partially sodiated Na3MoSe2 phase or product of side reactions, for example, SEI layer formation. At the end of charge process, we found in the electrode the co-existence of three phases: Mo, Se and Na2MoSe2 which take part in subsequent reactions.

At the beginning of the 2st discharge MoSe2 structure exists and according to XPS contains some extra sodium in form of Na2MoSe2 phase. Therefore, the intercalation, then conversion, processes (Na3MoSe2, then Mo + Na2Se) are expected. However, the existence of Se at the beginning of sodiation leads to the alloying reaction between Na+ and Se, which can run simultaneously to intercalation and conversion processes. The products of 2nd discharge include Mo and Na2Se formed in conversion and alloying reactions. According to similar CV curves, 2nd charge goes in a similar way to 1st charge, where Na2Se phase is dealloyed and MoSe2-type structure is reconverted. Based on XANES analysis the products of 1st and 2nd cycles are the same. From the 2nd cycle on the further cycles go through the same mechanisms and discharging/charging process seems to be reversible according to symmetrical CV curves.

According to previously published considerations about chalcogenide materials, the first discharge process for both Li- and Na-ion batteries is supposed to be based on intercalation and conversion processes as in MoS2, 2102406 Since there is a much bigger availability of the data regarding the (de)insertion reactions for MoS2, it became a model example in general consideration of the processes in the whole chalcogenides group. The similar structure and properties of selenium and sulfur are very suggestive, so the same mechanism was proposed. Since the theory about intercalation and conversion mechanisms during 1st discharge was taken as an assumption, the exact transitional reactions taking place in MoSe2 electrode during initial sodiation have never been studied.

Up to now, ongoing discussion on MoSe2 was only focused on the final product of 1st charging and brought up two theories, which seemed to be mutually exclusive. The first one predicted the formation of Mo and Na2Se during the sodiation process and the reformation of MoSe2 phase during charging. The second one assumes Mo and Se precipitation as products of charging. However, our results prove that the actual process includes both scenarios. We can clearly state that in the charge state after the 1st (de)insertion cycle all Mo, Se and Na₂MoSe₂ phases co-exist, which basically suggests that nature of the (de)sodiation mechanism is more complex than presented so far, also for MoS2. The results of our studies on electrochemical phase evolution suggest that Se, which is precipitated from the material during sodiation reaction, triggers the alloying mechanism with Na+ ions. Thus, during the operation of MoSe2 all three types of reactions: intercalation, conversion, and alloying occur. In further cycles, the starting point for intercalation reaction is IT-Na2MoSe2 type structure, which differentiates it from the first discharge. Reformation to IT phase in place of 2H is favorable due to its better transport properties.

Three considered stages of Na storages mechanism (intercalation, conversion and alloying) correspond to three reduction and oxidation peaks (I-II-III and I’-II’-III’) on CV curves for further cycles (Figure 6c). Taking into account calculated equilibrium voltage of Na-Se alloying reactions which are ≈1.8 V,2102406 we assigned reaction 1 as alloying. Consequently, we suspect that the order of reactions during work of the cell is as follows: alloying (I), intercalation (II), and conversion (III). Moreover, after analyzing the cyclic voltammograms at different scan rates we found that peaks I and I’ have the smallest potential shift. Thus, the highest kinetic was ascribed to the alloying process where Se reacts with Na+ ions. From this perspective, the promotion of the alloying process driven by Se precipitation enhanced both observed discharge capacity (due to new redox pair in the system Se⁰/Se²⁻) and the kinetics of the electrode.

4. Conclusion

MoSe2 with snowballs morphology and hexagonal 2H structure was successfully synthesized via the hydrothermal method. Up to now, intercalation and conversion mechanism of 1st discharge of MoSe2 in Na-ion cell was proposed mainly based on similarity to well-known MoS2. By means of operando XRD, EIS, XPS, and XANES analysis we discovered additional alloying reactions taking place simultaneously to intercalation-conversion processes during first discharge and charge processes. We proved that MoSe2 did not return to the initial crystal structure after a violation of its structure by complex electrochemical reactions with sodium ions. It was found that, after the first discharge-charge cycle, the MoSe2 evolves to more complex system being a mixture of Se, Mo, and 1T-structured Na2MoSe2. We observed that such a phase composition ensures a multi-way mechanism, composed of alloying, intercalation, and conversion processes, in further cycles, leading to high discharge capacities and low capacity fade during cycling. The galvanostatic charge/discharge tests shows that, MoSe2 exhibit high coulombic efficiency and capacity equal 320 mAh g⁻¹ even after 50 cycles. Such an abnormal phenomena of selenium precipitation was found to be exclusive among all chalcogenides and contribute to the high capacity of the selenide systems. Moreover, we suspect that the highest electrode reaction kinetic is ascribed to the alloying process where Se reacts with Na+ ions. Those observations are opening new routes for obtaining novel chalcogenides based anodes for SIBs with enhanced electrochemical properties and enrich general understanding of the (de)sodiation reactions in chalcogenide compounds.

5. Experimental Section

MoSe2 was synthesized via the hydrothermal method. In the first step, a stoichiometric amount of selenium powder (99.5% Acros Organics) was dissolved in hydrazine hydrate 50–60% (99.99%, Sigma Aldrich) and stirred for 2 h at room temperature until a clear red solution being obtained. Meanwhile sodium molybdate (98%, Sigma Aldrich) was dissolved in 4:1 solution of deionized water and ethylenediamine (99.5%, Sigma Aldrich) in another flask. Both mixtures were transferred to a Teflon-lined autoclave and stirred together at 300 rpm for 20 h at
160 °C. After cooling down to room temperature, the substrate was filtered using a Buchner funnel and thoroughly washed with deionized water and ethanol. Finally, the powder was heated in a vacuum oven at 80 °C for 24 h. In order to obtain well-crystallized MoSe2, the powder was annealed at 600 °C for 2 h with the Ar+5%H2 gas flow.

Phase purity and crystal structure of MoSe2 were investigated by means of X-ray diffraction using PANalytical Empyrean diffractometer with CuKα radiation in 2θ range. Structural characterization was conducted using Rietveld refinement in GSAS2 software. The microstructure and morphology were examined using a field emission SEM FEI NOVA NANO SEM 200. Energy-dispersive X-ray mapping was applied to estimate the chemical composition and to verify the distribution of the elements. The micro-Raman measurements were registered in Thermo Scientific DXR3 equipment. Analysis of the samples by micro-Raman spectroscopy was performed under ambient conditions. The pump radiation was supplied by a laser operating at a wavelength of 532 nm.

Electrochemical measurements were conducted in CR2032-type cells assembled in the glove box. Metallic sodium was used as a counter electrode and Whatman GF/D glass fiber as a separator. The electrolyte was NaPF6 (Alfa Aesar, 99.99%) dissolved in 2-methoxyethyl ether dispersing device, the slurry was cast on a metal collector and dried at 80 °C in a vacuum oven for 1 h to remove the remaining NPF6. After initial drying, the disc shaped-electrodes with a diameter of 15 mm were punched and further heated at 120 °C on a hot plate in an argon-filled glovebox (Braun, O2 and H2O <1 ppm) for 12 h to provide proper binding of PVDF.

Electrochemical measurements were conducted in CR2032-type cells assembled in the glove box. Metallic sodium was used as a counter electrode and Whatman GF/D glass fiber as a separator. The electrolyte was NaPF6 (Alfa Aesar, 99.99%) dissolved in 2-methoxyethyl ether (Diglyme, Alfa Aesar, 99%). Galvanostatic sodium insertion/extraction was performed using Biologic SP-300 potentiostat at 0.2 A g\(^{-1}\). After the homogenization step using a Polytron PT2000E, the slurry was cast on a metal collector and dried at 80:10:10. After the homogenization step using a Polytron PT2000E, the slurry was cast on a metal collector and dried at 80:10:10. After the homogenization step using a Polytron PT2000E, the slurry was cast on a metal collector and dried at 80:10:10.

Changes in crystal structure during electrochemical sodiation/desodiation were monitored using operando XRD which was performed in 10°–90° range. Structural characterization was conducted using Rietveld refinement in GSAS2 software. The microstructure and morphology were examined using a field emission SEM FEI NOVA NANO SEM 200. Energy-dispersive X-ray mapping was applied to estimate the chemical composition and to verify the distribution of the elements. The micro-Raman measurements were registered in Thermo Scientific DXR3 equipment. Analysis of the samples by micro-Raman spectroscopy was performed under ambient conditions. The pump radiation was supplied by a laser operating at a wavelength of 532 nm.

Changes in MoSe\(^2\) structure at various degrees of sodiation were investigated using ex situ techniques (XRD, XPS, XAS) on electrode layers recovered in the glove box and protected during transfer to reduce contact with the atmosphere.

To observe changes in the oxidation state of molybdenum and selenium at various states of sodiation, XPS technique was carried out using X-ray photoelectron spectroscopy (XPS). The measurement was performed at the KEK-PAL beamline, Synchrotron Radiation Research, Japan. The XPS measurements were performed at the KEK-PAL beamline, Synchrotron Radiation Research, Japan. The XPS measurements were performed at the KEK-PAL beamline, Synchrotron Radiation Research, Japan. The XPS measurements were performed at the KEK-PAL beamline, Synchrotron Radiation Research, Japan.

In situ EIS measurements were performed to estimate changes in both charge transfer resistance and sodium chemical diffusion coefficient as a function of the state of sodiation. The procedure consisted of three steps: discharging the cell at 0.2 A g\(^{-1}\) current rate for 1 h, relaxing the cell in open circuit conditions, applying AC voltage with an amplitude of 10 mV over 10 mHz to 1 MHz frequency range.

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

### Acknowledgements
The work was supported by the National Science Centre Poland on the basis of the decision number 2016/21/D/ST5/01658. Part of the work was realized using the infrastructure of the Laboratory of Conversion and Energy Storage Materials in the Centre of Energy AGH subsidy grant number 16.16.210.476. The XAFS measurements were performed at the PEEM/XAS beamline, SOLARIS National Synchrotron Radiation Centre, Poland (Proposal Number 201057).

### Conflict of Interest
The authors declare no conflict of interest.

### Data Availability Statement
Research data are not shared.

### Keywords
alloying mechanism, conversion reaction, MoSe\(_2\), Na-ion batteries, Se L-edge, transition metal chalcogenides

Received: March 11, 2021
Revised: April 22, 2021
Published online: May 24, 2021

[1] M. Armand, J. M. De Ilarduya, L. Otaegui, J. M. López del Amo, J. Power Sources 2017, 337, 197.
[2] A. Plewa, A. Kulka, Ł. Kondracki, Ł. Lu, J. Molenda, J. Power Sources 2019, 419, 42.
[3] A. Kulka, C. Marino, K. Walczak, C. Borca, C. Bolli, P. Novák, C. Villevieille, J. Mater. Chem. A 2020, 8, 6022.
[4] D. Yuan, X. Hu, J. Qian, F. Pei, F. Wu, R. Mao, X. Ai, H. Yang, Y. Cao, Electrochim. Acta 2014, 116, 300.
[5] A. Plewa, A. Kulka, E. Hanc, W. Zajać, J. Sun, L. Lu, J. Molenda, J. Mater. Chem. A 2020, 8, 2728.
[6] Y. Zhao, X. Cao, G. Fang, Y. Wang, H. Yang, S. Liang, Chem. Eng. J. 2018, 339, 162.
[7] H. Li, Z. Zhang, M. Xu, W. Bao, Y. Lai, K. Zhang, J. Li, ACS Appl. Mater. Interfaces 2018, 10, 24564.
[8] M. J. Piernas-Muñoz, E. Castillo-Martínez, O. Bondarchuk, M. Armand, T. Rojo, M. J. Piernas-Munoz, E. Castillo-Martínez, O. Bondarchuk, M. Armand, R. Teofilo, J. Power Sources 2016, 324, 766.
[9] H. Wang, L. Wang, S. Chen, G. Li, J. Quan, E. Xu, L. Song, Y. Jiang, J. Mater. Chem. A 2017, 5, 3569.
[10] Y. Liu, X. Liu, T. Wang, L. Z. Fan, L. Jiao, Sustainable Energy Fuels 2017, 1, 986.
