Molybdenum Dichalcogenide Cathodes for Aluminum-Ion Batteries

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Many successful battery electrodes are based on 2D-layered materials. Aluminum-ion batteries are studied using molybdenum dichalcogenides: MoS$_2$, MoSe$_2$, and MoSSe as active cathode materials. The batteries show clear discharge voltage plateaus in the ranges 1.6–1.4 V for MoS$_2$ and MoSe$_2$, and 0.6–0.5 V for MoSSe. MoS$_2$ and MoSe$_2$ have similar crystal structures; interestingly, it is found that MoSe$_2$ performed better than MoS$_2$. MoSSe exhibits a higher specific capacity over MoS$_2$ and MoSe$_2$, but the energy density is lower than MoSe$_2$ at a current rate of 40 mA g$^{-1}$. MoSe$_2$ cells record a discharge capacity of $\approx$110 mAh g$^{-1}$ with an average potential in the range of 2.0–1.8 V and 1.5–0.8 V during discharge. The cells are stable at 100 mA g$^{-1}$ for over 200 cycles with 90% coulombic efficiency.

1. Introduction

Aluminum-ion batteries (AIBs) offer an alternative to the prevalent lithium-ion battery (LIB) technology. Aluminum being the most abundant metal in the Earth’s crust, these batteries will not only be much cheaper, but hold promise to solve other problems such as recyclability and thermal runaway. Furthermore, the multivalent nature of aluminum may result in a higher specific capacity and energy density compared with other monovalent battery types. Research on AIBs is still in its early stages, and the current work focuses mainly on electrolytes and cathode materials. In this article, we explore different molybdenum dichalcogenide-based materials and their mechanism of energy storage. We expected that 2D-layered materials that support intercalation of charged species might be suitable as active cathode materials in AIBs.[1,2]

The most common AIB electrolyte is currently the ionic liquid 1-ethyl-3-methylimidazolium/tetrachloroaluminate (EMIm$^+$/AlCl$_4^-$), although many other alternatives are under investigation.[3] The most studied cathode types are graphite-based, where chloroaluminate ions AlCl$_4^-$ have been shown to intercalate/deintercalate during the charging/discharging processes. Various forms of graphite such as fluorinated graphite,[4] Kish graphite flakes,[5] 3D graphite foam,[6] few-layer graphene aerogels,[7] and several others have been tested. Analytical techniques such as X-ray diffraction (XRD), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) have been used broadly to verify the intercalation/deintercalation mechanism.

Molybdenum dichalcogenides (MoX$_2$ where X = S, Se, or Te) display similar properties as graphite. They have a 2D-layered structure, which allows intercalation of ions and is electrically conductive. Lower volumetric expansion on cycling is an advantage these materials have over graphite cathodes.[8,9] Among various transition metal chalcogenides, MoS$_2$ has been extensively studied as a cathode for rechargeable batteries,[10–13] making them attractive candidates for AIB cathodes. In 2015, Geng et al. found that Al$^{3+}$ ions fully intercalated into chevrel phase Mo$_6$S$_8$ with the cations occupying two different sites in the crystal lattice.[14] This mechanism was called the “rocking chair” mechanism where charge-carrying species shuttled back and forth between intercalating electrodes during cycles, whereas the overall electrolyte concentration remains constant. The discharging and charging reactions at the anode (Equation (1)) and cathode (Equation (2)) were proposed as follows:

\begin{align}
\text{Al} + 7\text{AlCl}_4^- &\rightarrow 4\text{Al}_2\text{Cl}_7^- + 3e^- \quad \text{(1)} \\
8\text{AlCl}_7^- + 6e^- + \text{Mo}_6\text{S}_8 &\rightarrow \text{Al}_2\text{Mo}_6\text{S}_8 + 14\text{AlCl}_4^- \quad \text{(2)}
\end{align}

Three years later, Li et al. prepared MoS$_2$ microspheres by a simple hydrothermal method.[15] They proposed a similar mechanism where Al$^{3+}$ ions inserted into the electrode accompanied by a phase transformation at the electrode interface. Li and his group confirmed this phase transition by using ex situ XPS and XRD etching techniques. The reaction equations for this battery system at the cathode (Equation (3)) and anode (Equation (4)) were proposed as follows:

\begin{align}
\text{MoS}_2 + x\text{Al}^{3+} + 3xe^- &\rightarrow \text{Al}_x\text{MoS}_2 \quad \text{(3)} \\
\text{Al} + 7x\text{AlCl}_4^- &\rightarrow 4x\text{Al}_2\text{Cl}_7^- + 3xe^- \quad \text{(4)}
\end{align}

In general, these cells showed low energy density and had reversibility issues in the redox processes. It has been reported that transition metal dichalcogenide electrodes tend to transition
from a 2H phase into a more conducting 1T phase when used in a battery.[16] A hybrid Mg\(^{2+}/\)Li\(^+\) cell was tested using bulk MoS\(_2\) as a cathode material. During cyclic voltammetry (CV) scans, the authors associated the first cathodic peak, with a phase transition. 2H phase MoS\(_2\) was converted to 1T phase during initial ion intercalation. This seems to be a common phenomenon for molybdenum dichalcogenides, since Li et al. observed similar transitions in sodium ion batteries.[17,18] It mostly takes place during the first cycle and because the phase change is irreversible, it can be detected in a cyclic voltammogram.

In this work, we studied a range of 2D molybdenum dichalcogenides including MoS\(_2\), MoSe\(_2\), and MoSSe, and tested them as cathodes for nonaqueous AIBs. Our unpublished, preliminary density functional theory (DFT) calculations indicated a significant decrease in interlayer spacing of these materials when Al\(^{3+}\) cations were assumed to intercalate (owing to the very high charge density of Al\(^{3+}\)). Therefore, we propose intercalation of structurally distorted AlCl\(_4^-\) anions into the cathode layers. Surprisingly, we found that MoSe\(_2\)-based cathodes performed different and better than all of the other molybdenum dichalcogenides.

2. Results and Discussion

Figure 1 shows the crystal structure of MoX\(_2\), where X is sulfur (S) and/or selenium (Se). The material has two vacant sites for intercalation—M1 and M2. M1 denotes the spaces in between the X–Mo–X atoms, whereas M2 represents the space created between the MoX\(_2\) layers, as shown in Figure 1a. The interlayer distance in MoX\(_2\) is 6.3 Å with a gallery height of 3 Å. The layers are held together by weak van der Waals (vdW) forces. M2 presents an open network and provides various interstitial sites for intercalation. As AlCl\(_4^-\) ions are 5.28 Å in diameter, as reported by Takahashi et al.,[19] they undergo some distortion during intercalation to fit into these layers. Our preliminary results showed that Al\(^{3+}\) would contract the MoX\(_2\) layers when trying to intercalate, making AlCl\(_4^-\) anion intercalation more likely. Also, the triply charged Al\(^{3+}\) cation has to overcome strong electrostatic forces from the S\(^2-\) or Se\(^2-\) anion network to enter, making the intercalation process slow and most likely not reversible. Therefore, we propose intercalation of AlCl\(_4^-\) anions from the electrolyte into M2 sites of MoX\(_2\) during charge. Galvanostatic cycles, CV, XRD, Raman spectra, and XPS results discussed later, strongly support our claim of a reversible intercalation process especially in MoSe\(_2\).

A modified two-electrode polyether ether ketone (PEEK) cell (Figure 2) was used for conducting preliminary electrochemical tests. Cathode preparation, electrolyte synthesis, and cell configuration are described in Section 4.

Figure 3a–c shows the charge/discharge cycles (CDCs) for MoS\(_2\), MoSe\(_2\), and MoSSe at a current rate of 40 mA g\(^{-1}\). The discharge capacity of MoS\(_2\) in its first cycle was found at \(\approx 45\) mAh g\(^{-1}\) (Figure 3a). Comparing this with its first CV scan (Figure 3a, inset), a good correlation between the discharge voltage plateau and reduction peaks, and other redox features was found. The voltage bend during discharge at 2.0 V matched well with the reduction peak at 2.0 V. The other reduction peak at 1.0 V, however, did not correspond to any of the other peaks.

With discharge voltage bends between 2.0–1.8 and 1.5–0.8 V, the first CV scan for MoSe\(_2\) displayed two reduction peaks at 1.65 V (point A) and 1.0 V (point B) (Figure 3b, inset). The peak at 1.0 V suggested an irreversible reaction because this peak was absent in the following scans. Based on this, we agree with Li et al.’s interpretation and attributed this peak to an irreversible phase transition.[17] During this transition, the semiconducting 2H phase converted into a more metallic 1T phase. This transition seemed to increase the interlayer spacing of MoSe\(_2\) by reducing the vdW forces that exist between the two layers.[16] Al/MoSSe cells showed three distinct plateaus during charge at 1.2, 2.0–2.1, and 2.3–2.4 V in its first cycle, with a discharge plateau at 0.5 V, as shown in Figure 3c. Capacities of all molybdenum dichalcogenides were recorded at different current rates of 25, 40, and 100 mA g\(^{-1}\), and shown in Figure 3d. As MoSe\(_2\) displayed stable specific capacities at all current rates, we recorded further 200 cycles at a high current rate of 100 mA g\(^{-1}\). A highly reversible electrochemical reaction was observed because the capacity remained at \(\approx 35\) mAh g\(^{-1}\) after 200 cycles (Figure 3e) at 100 mA g\(^{-1}\). The presence of multiple
charging plateaus in MoSe₂ might correspond to various oxidation processes occurring when AlCl₄⁻ interacts individually with S and Se atoms. The first CV scan (Figure 3c, inset) showed an irreversible reduction potential at 0.9 V, point B', like MoSe₂, implying a similar phase transition. It seems MoSSe undergoes a lattice distortion and the material loses its long-range order after converting to its 1T phase. This might be the reason why the cells fail to deliver a stable capacity. In addition, a significant difference was observed charge/discharge curves of all the molybdenum dichalcogenide cathodes—similar to what was previously reported by Li et al. in 2018.[5] Electrochemical polarisation at the electrode interface might be responsible for the uneven potentials. Formation of an insulating layer on the cathode surface by the new Al–MoX₂ complexes might have attributed to the overpotential.

Electrochemical performance of a blank cell with an uncoated Mo foil (Figure S11. Supporting Information) showed that the current collector did not contribute to the cell’s capacity. Both MoS₂ and MoSe₂ have similar interlayer distance (6.3 Å) and a gallery height of 3.0 Å. However, MoSe₂ showed a higher capacity and a more stable cycle life. To account for this behaviour, we compared the CVs of all electrodes at a scan rate of 10 mV s⁻¹, as shown in Figure 4. Different charge storage mechanisms lead to distinct features in the CVs. Ideal capacitors result in a rectangular CV shape. Due to the absence of Faradaic processes, the charging/discharging currents become directly proportional to the scan speed. Batteries show oxidation and reduction peaks in their voltammograms because the charge storage takes place via reversible redox processes.[6] We observed that the CVs of MoS₂ and MoSSe in Figure 4b,c covered a broader area, suggesting an additional capacitor-like charge storage mechanism. The non-Faradaic process taking place at the surfaces of MoS₂ and MoSSe might have added to their original capacity values. Also, the peak indicating phase transition from 2H → 1T at ≈0.9–1.0 V was visible only for MoS₂ and MoSSe. Therefore, it can be concluded that the charge storage in MoS₂ is primarily based on reversible oxidation and reduction of Mo from Mo⁶⁺ to Mo⁴⁺ with oxidation peaks visible at 1.8 V (O₁) and 2.1 V (O₂), and a corresponding reduction peak at 2.0 V (R₁) (Figure 4a). Two more reduction peaks were found at 1.6 V (R₂) and 0.9 V (R₁). However, their peak intensities decreased with every scan. CV scans of Al/MoS₂ cells in Figure 4b indicated a reversible electrochemical process, which was in agreement with their CDCs. The scans overlapped with each other displaying two oxidation peaks at 1.7 V (O₁’ and O₂’) and 2.1 V (O₂’) and corresponding reduction peaks at 1.8 V (R₁’) and 1.6 V (R₂’). In Figure 4c, an oxidation and a reduction peak at 1.7 V (O₁”) and 1.8 V (R₁”) was observed for Al/MoSSe, respectively. R₁'’s peak intensity increased after every scan, which might suggest sluggish kinetics in the system—perhaps due to strong interaction between the positive metal ion and the intercalating anion. The voltammogram became more capacitor-like after a few scans, indicating the absence of reversible redox processes. The phenomena indicate that an initial intercalation of anions into the layers of MoSSe was followed by surface adsorption of AlCl₄⁻ anions.

Figure 5 shows the XRD patterns of MoS₂, MoSe₂, and MoSSe electrodes. Pristine (in black), charged (in green), and discharged (in red) cathodes were compared after 30 cycles each. MoS₂ cells displayed a very small shift in their d-spacings. The peak at 14.2° for 002 plane (6.22 Å) shifted to 14.0° (6.32 Å), as shown in Figure 5a. Most of the peaks retained their positions after charge and discharge showing no significant change in the lattice dimensions. A completely different XRD pattern appeared after charging for Al/MoSe₂ cells, as new peaks appeared at 2θ values, as shown in Figure 5b. Diffraction peaks of 002, 100, 110, and 008 planes reappeared after discharge. Every time the cells were charged, MoSe₂ seemed to adopt this new crystal lattice. However, the characteristic peaks of MoSe₂ reappeared after discharge. This follows closely the observations made by Rani et al., where they proved intercalation of ions into the layers of fluorinated natural graphite during charging using XRD data.[7] This strongly confirms our hypothesis of a reversible intercalation taking place in MoSe₂. It was interesting to note that MoSSe did not have a well-defined crystal structure to begin with (Figure 5c). The patterns after charge and discharge did not look any different from the untested cathode. This confirmed MoSSe layers did not undergo any significant expansion and the initial specific capacities at ≈250 mAh g⁻¹ came from the non-Faradaic reactions via electrostatic absorption of the AlCl₄⁻ anions onto the electrode’s surface. Furthermore, the material underwent irreversible changes resulting in cathode degradation after a few cycles. The images obtained from the scanning electron microscope (SEM) have been shown in Figure S12, Supporting Information. While MoS₂ and MoSe₂ displayed a layered structure in Figure S12a,b, Supporting Information, respectively, MoSSe lacked a long-range order. The diffraction patterns of all the Al–Mo–Se complexes present in the International Centre for
Diffraction Data (ICDD) database have been compared with the new complex shown in Figure 5.

To further understand the interactions between AlCl$_2$/C$_{25}$ and MoSe$_2$, we used XPS, which is a useful method for distinguishing various oxidation states and helps in identifying different polymorphs (2H and 1T). The detailed narrow spectrum scans in Figure 6 show the binding energies of Mo (3$d_{5/2}$ and 3$d_{3/2}$ in Figure 6a,b) and Al 2p peaks for charged MoSe$_2$ (Figure 6c) and MoSSe electrodes (Figure 6d). In pristine MoSe$_2$, two peaks appeared at 229.1 and 232.2 eV corresponding to 3$d_{5/2}$ and 3$d_{3/2}$ (Figure 7a). Selenium displayed a doublet at 55.4 and 54.6 eV corresponding to Se 3$d_{3/2}$ and 3$d_{5/2}$, respectively (Figure 7c). Peak splitting in an XPS spectrum can indicate a phase change or a change in oxidation state of the said element. After charge, the peak for Mo 3d split into three doublets, indicating the presence of multiple oxidation states or phases of Mo (Figure 6a). Se 3d deconvoluted into four peaks after charge (Figure 7e), confirming the presence of more than one phase after charge. This was similar to observations made by Fan et al. where they used MoS$_2$/graphene cathode in a hybrid Mg$^{2+}$/Li$^+$ cell. Pristine electrodes of MoSSe contained Mo in more than one oxidation state, and provided evidence for the presence of both 2H and 1T polymorphs (Figure 7b). After charging, the width of peaks at 231.7 eV (Mo 3$d_{3/2}$, in green) and 228.6 eV (Mo 3$d_{1/2}$, in green) increased, as shown in Figure 6b. After comparing Figure 7d,f, we noted that the Se 3d spectrum deconvoluted into four peaks after charging the MoSSe cells. An increase in the peak width was observed for both Mo and Se binding energies. A new peak at ≈236 eV in Mo 3d spectra (in blue) for MoS$_2$, MoSe$_2$, and MoSSe electrodes was assigned to Mo$^{6+}$ species typically present in molybdenum oxide, MoO$_3$. 
Figure 4. Cyclic voltammograms of a) MoS$_2$, b) MoSe$_2$, and c) MoSSe at a scan rate of 10 mV s$^{-1}$ in a two-electrode aluminum-ion cell against an Al/Al$^{3+}$ reference electrode.

Figure 5. XRD patterns of pristine (black), charged (green), and discharged (red) a) MoS$_2$, b) MoSe$_2$, and c) MoSSe electrodes charged to 2.35 V and discharged to 0.2 V versus Al/Al$^{3+}$, with ICDD references, in blue.
The presence of new peaks and peak shifts that were detected in Mo 3d spectra for charged MoS$_2$ and MoSe$_2$ cathodes were not observed in MoSSe (cf. Figure 6a, 7a, and 8a,b). This further confirms the absence of redox reactions and that the capacity was mainly derived from a surface-based charge storage. As expected, a general trend was observed for all the three cathodes, where the charged electrodes showed higher concentration of aluminum and chlorine than discharged electrodes, as shown in Figure 7g,h. The XPS spectra support the observation that MoSe$_2$ underwent a phase transformation that made it a better performing cathode than MoS$_2$. Further analysis is needed to fully understand the mechanism of MoSSe.

Charged MoSe$_2$ electrodes displayed binding energies of Al 2p at 77 eV (in red) and 76 eV (in blue) corresponding to chlorides Al$_x$Cl$_y$ and Al$_2$O$_3$, respectively, in Figure 6c. New peaks were observed at much lower binding energies—69 and 70 eV (in green) suggesting the presence of a new complex with an increased electron density around aluminum. An overall spectra of charged MoS$_2$, MoSe$_2$, and MoSSe cathodes is shown in Figure 6e, indicating the presence of Al and Cl (from chloroaluminates) and oxygen (from MoO$_3$).

In addition, we compared the Raman spectra of pristine and charged cathodes to detect shifts in vibrational modes shown in Figure 9. Yang et al. and Sharma et al. have reported that $E_{12g}$ and $A_{1g}$ are the most intense vibrational modes for molybdenum dichalcogenides.$^{[21–23]}$ Peaks corresponding to $E_{12g}$ and $A_{1g}$ modes for MoS$_2$ (Figure 9a) are prominent at 384.6 and 410.2 cm$^{-1}$, respectively. $A_{1g}$ indicates an out-of-plane symmetric displacement of S atoms, whereas $E_{12g}$ suggests an in-layer displacement. Also, separation between the two peaks indicates a multilayer structure, which was observed for all three materials. No significant peak shift or peak broadening was observed for the charged MoS$_2$ electrode. For 2H MoSe$_2$ (Figure 9b), $A_{1g}$ is the most intense vibration occurring at a frequency lower than that

Figure 6. XPS spectra of Mo 3d orbitals in a charged a) MoSe$_2$ and b) MoSSe cathode and Al 2p orbitals in a charged c) MoSe$_2$ and d) MoSSe cathode. e) An overview spectrum of all three tested and charged cathodes.
of $E_{2g}^{1}$. When the number of layers decreases, the $A_{1g}$ mode softens and an increase in full-width-at-half-maximum (FWHM) is detected. Spectra generated after intercalation were different from the pristine cathodes because phase conversion from 2H to 1T decreases the molecule’s symmetry and more Raman bands get active. The presence of $J_{1}$ and $J_{2}$ peaks in addition to $E_{1g}$ and $A_{1g}$ at lower wavelengths suggest the existence of 1T phase especially for MoSe$_2$ and MoSSe (inset, Figure 9b,c). This agrees with the CV scans and XPS results where a phase transition was observed for MoSe$_2$ and MoSSe. Raman results suggest that the symmetry and vibrational modes of MoSe$_2$’s crystal lattice changed after repeated cycles. It seems that the

Figure 7. XPS spectra of Mo 3d for pristine a) MoS$_2$ and b) MoSSe electrodes. MoS$_2$ spectra consists of two peaks at 232.2 and 229.1 eV, corresponding to Mo$^{4+}$. MoSSe spectra consist of three doublet bands, which are assigned to Mo$^{4+}$, one with oxidation state between 4 and 6, and another band corresponding to Mo$^{5+}$ at 236 eV. Se 3d orbital spectra for pristine c) MoSe$_2$ and d) MoSSe. Se from MoSe$_2$ observed peaks corresponding to 3d$_{3/2}$ and 3d$_{5/2}$ at 55.6 and 54.6 eV, respectively. Binding energies of Se 3d from charged e) MoSe$_2$ and f) MoSSe cathodes. Binding energies of g) Al 2p and h) Cl 2p in the charged and discharged cathodes—a general trend followed by all molybdenum dichalcogenides.
Figure 8. XPS spectra of Mo 3d and S 2s orbitals in a) a charged and b) discharged MoS$_2$ cathode and binding energies of S 2p orbital in c) a charged and d) discharged MoS$_2$ cathode.

Figure 9. Raman spectra of pristine (black) and charged (green) a) MoS$_2$, b) MoSe$_2$, and c) MoSSe electrodes with position of new Raman active J1 and J2 bands marked along with $E_{1g}$ and $A_{1g}$ bands.
phase transformation occurring in the first few cycles for MoSe$_2$ changes its structure in a way that allows it to intercalate more AlCl$_4$ anions resulting in a higher capacity than MoS$_2$, despite both of them having a similar structure. First-principle studies on both materials shall confirm this hypothesis.

3. Conclusions

In this work, we studied systematically the charging/discharging mechanism of AlIBs, using different molybdenum dichalcogenide cathodes. It was found that MoSe$_2$ showed a higher capacity and cyclic stability than MoS$_2$ and MoS$_2$. CV and XPS results indicated an irreversible phase transition to a more metallic 1T phase. This transition worked in favour of MoSe$_2$ and its capacity increased. XRD, XPS, and Raman results supported the hypothesis that AlCl$_4$ intercalated reversibly into MoSe$_2$. An additional electrocapacitative behaviour was observed in MoSe$_2$ that added to its overall capacity. The cells delivered a potential of $\approx2.0\,\text{V}$ with discharge capacity of 30 mA h g$^{-1}$ with nearly 95% coulombic efficiency at a current rate of 100 mA g$^{-1}$.

4. Experimental Section

Cathode Preparation: A slurry was prepared by mixing MoX$_2$ (85% by wt.), 9% binder (PVDF, MTI Corporation) and 6% Super-P conductive carbon (99%+% metals basis, Alfa Aesar) in N-methyl pyrrolidone (NMP) (anhydrous, 99.5%, Sigma-Aldrich). This slurry was ‘doctor-bladed’ onto molybdenum foil (thickness 0.1 mm, MTI Corporation) and dried in a vacuum oven at 120 °C for 12 h to adhere the slurry on the conductive substrate and evaporate the solvent. The specific loading of the active materials was approximately 12 mg cm$^{-2}$.

Electrolyte Preparation: Anhydrous AlCl$_4$ (Sigma-Aldrich) and EMImCl (97%, Sigma-Aldrich) were mixed in a molar ratio of 1.3:1, at room temperature. EMImCl was baked in vacuum for 24 h at 100 °C to remove residual moisture. Small aliquots of AlCl$_4$ were added to EMImCl after every few minutes until the white fumes settled down. The ionic liquid was stirred for 2–3 h until a clear brown liquid was obtained. As the electrolyte was hygroscopic in nature, it was prepared in a N$_2$-filled glove box with $<0.1$ ppm H$_2$O/O$_2$.

Cell Assembly: PEEK cells were used for preliminary electrochemical tests. Molybdenum rods were used as plungers to push in the electrodes as close to each other. Active material coated on molybdenum foil was used as the cathode and placed at bottom of the cell. As this was a two-electrode setup, aluminum foil was used as both counter and reference electrode. We used Mo foil because nickel and steel showed reactivity toward the ionic liquid electrolyte and reduced its potential window. Glass microfibers (Grade GF/F, Whatman) were used as separators. An 80 μL of the electrolyte was used to wet the separator. Aluminum foil (thickness 0.1 mm, 99%, GoodFellow) was used as an anode and placed on top of the separator. The cell was then sealed and wrapped with a paraffin to avoid any further air or moisture contact after it was taken out of the glove box.

Supporting Information

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

Conflict of Interest

The authors declare no conflict of interest.

Keywords

aluminum-ion batteries, electrochemistry, layered compounds, molybdenum dichalcogenide cathodes

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