Research Article

Enhanced Structural Integrity and Electrochemical Performance of AlPO₄-Coated MoO₂ Anode Material for Lithium-Ion Batteries

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AlPO₄ nanoparticles were synthesized via chemical deposition method and used for the surface modification of MoO₂ to improve its structural stability and electrochemical performance. Structure and surface morphology of pristine and AlPO₄-coated MoO₂ anode material were characterized by electron microscopy imaging (SEM and TEM) and X-ray diffraction (XRD). AlPO₄ nanoparticles were observed, covering the surface of MoO₂. Surface analyses show that the synthesized AlPO₄ is amorphous, and the surface modification with AlPO₄ does not result in a distortion of the lattice structure of MoO₂. The electrochemical properties of pristine and AlPO₄-coated MoO₂ were characterized in the voltage range of 0.01–2.5 V versus Li/Li⁺. Cyclic voltammetry studies indicate that the improvement in electrochemical performance of the AlPO₄-coated anode material was attributed to the stabilization of the lattice structure during lithiation. Galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) studies reveal that the AlPO₄ nanoparticle coating improves the rate capability and cycle stability and contributes toward decreasing surface layer and charge-transfer resistances. These results suggest that surface modification with AlPO₄ nanoparticles suppresses the elimination of oxygen vacancies in the lattice structure during cycling, leading to a better rate performance and cycle life.

1. Introduction

Lithium ion batteries are extensively used in a variety of portable electronic devices due to their high power density and long cycle life [1]. As reported, they are critically important for electric/hybrid vehicles as the power storage of the future [2]. Therefore, lithium ion batteries have attracted much interest in the field of fundamental study and applied research. Most commercialized lithium ion batteries use graphite as an anode material due to its accessibility and low cost; but its theoretical capacity is only 372 mAh·g⁻¹ calculated by forming the compound of LiC₆ and cannot meet the ever-increasing demands for high capacity lithium ion technology [3]. By replacing graphite with transition metal oxides as anode materials, the capacity is enhanced. This is due to their close packed oxygen array, providing a framework structure and specific site for topotactic insertion and removal of lithium ions during charge/discharge process. A number of transition metal oxides have been studied and reported so far, including Mn₃O₄, Co₃O₄, MnO, TiO₂, NiO, MoO₂, and SnO₂, because of their possibility of various oxidation states and the search of new materials for energy storage [3, 4].

In order to improve structural stability and electrochemical behavior, many groups have demonstrated that the addition of a thin coating of metal phosphates, fluorides, oxides,
or other analogous materials onto the cathode particle results in reduced irreversible capacity, improved rate capability, and cycle life [5]. Surface modification of the electrode material by substitution is an effective method to improve the electrochemical properties [6]. Such substitutions are usually done for electrochemically active elements, causing lower capacity and Li$^+$ diffusion because the substitutions are usually electrochemically inactive ingredients. A coating approach is beneficial with respect to delivery of the initial capacity because there is no reduction of the amount of electrochemically active element in the electrode material. Therefore, a small amount of coating on the surface of electrode materials can improve the electrochemical properties [7–9]. The improvements in performance of these lithium ion cathodes by surface modification via the addition of coatings have been attributed to a diverse series of mechanisms, such as the coating promoting the retention of oxide ion vacancies in the crystal lattice after the first charge [10], suppression of the decomposition of the electrolyte [11], and the maintenance of low microstrain for better structural integrity and crystallinity during cycling [12].

Aluminum phosphate (AlPO$_4$), an environmentally friendly, lower cost, and thermally stable material, is of great interest in both environmental and technological fields [13]. With regard to the application of AlPO$_4$ for lithium ion batteries, other groups reported improvement concerning the safety and the electrochemical properties of the cathode materials by applying a direct coating of AlPO$_4$ nanoparticles from an aqueous solution [14–16]. Jiao et al. [17] successfully prepared AlPO$_4$-coated LiV$_2$O$_4$ powders by mixing active material LiV$_2$O$_4$ with AlPO$_4$ nanoparticle suspension followed by a low temperature heat treatment. The AlPO$_4$-coated material was found to reduce the capacity fading significantly. Manthiram and Wu [18] studied the effects of surface modification of Li$_x$MnO$_2$ and LiMO$_2$ (where M = Mn, Ni, and Co) solid solutions modified with 3 wt.% Al$_2$O$_3$, CeO$_2$, ZrO$_2$, SiO$_2$, ZnO, AlPO$_4$, and 0.05 atom F per formula unit and were characterized by XRD and charge/discharge measurements in lithium cells. Among all coating materials, results showed that the AlPO$_4$ modified sample had the largest reduction in irreversible capacity, compared to the rest of the samples modified with different coatings. Cho [19] reported that LiCoO$_2$ cathodes coated with AlPO$_4$ have improved their electrochemical performance due to the formation of homogeneous surface layers, in contrast with other coating materials (Al$_2$O$_3$ and ZrO$_2$).

Recently MoO$_2$, with a theoretical reversible capacity of $\sim$838 mAh g$^{-1}$, has received much attention and has been considered as a promising anode material in lithium ion batteries because of its low electrical resistivity, high electrochemical activity, and high chemical stability [20]. One of the intrinsic drawbacks of MoO$_2$ for lithium ion battery applications is its volume expansion during Li$^+$ insertion/extraction process. The irreversible volume change causes MoO$_2$ particles to pulverize and crack, causing the detachment of the active material from the current collector, and consequently leading to a substantial loss in capacity [21]. In this context, we hereby present a study of the effects of AlPO$_4$ nanoparticle coating on the structural and electrochemical properties of MoO$_2$ anode material.

2. Experimental

Commercially available high purity chemicals were directly used without further purification. Pristine MoO$_2$ powder (Molybdenum (IV) oxide, Sigma Aldrich) was sintered at 350°C for 2 hours and ground thoroughly with an agate mortar and pestle, until a fine and homogeneous powder was obtained. To prepare AlPO$_4$-coated MoO$_2$, stoichiometric amounts of aluminum nitrate nonahydrate (Al(NO$_3$)$_3$9H$_2$O-98%; Alfa Aesar) and ammonium hydrogen phosphate ((NH$_4$)$_2$HPO$_4$; Alfa Aesar) were dissolved separately in nanopure water. Ammonium hydrogen phosphate solution was slowly added to the aluminum nitrate nonahydrate solution until a white AlPO$_4$ nanoparticle suspension was observed. MoO$_2$ powder with an average particle size of $\sim$5 µm was added to the coating solution and stirred thoroughly for 2 hours. The amount of AlPO$_4$ in the solution was $\sim$3 wt. % of the MoO$_2$ powder. The solution was then filtered, dried at room temperature in air, and sintered at 400°C for 4 hours in flowing argon.

2.1. Electrode Preparation. Electrodes were prepared by spray coating Cu foil substrates with slurries of 90 wt.% anode powder, 5 wt.% carbon black (100% compressed, 99.5% metal basis; Alfa Aesar), and 5 wt.% PVDF binder (poly-vinylidene fluoride; Alfa Aesar) in 1-Methyl-2-pyrrolidinone (anhydrous, 99.5%; Sigma Aldrich). The pristine and AlPO$_4$-coated MoO$_2$ electrode materials were used as working electrodes. Coin cells were assembled inside an argon-filled glove box (M. Braun, USA) using stainless steel CR2032 coin cell hardware. Li metal foil was used as the counter and the reference electrode (0.75 mm thick × 19 mm wide, 99.9%, metal basis, Alfa Aesar). Electrodes inside the coin cell were separated using a Celgard 2400 membrane. Lithium hexafluoroarsenate (LiPF$_6$) dissolved in a 1:1 molar ratio solution of dimethyl carbonate (DMC) and ethylene carbonate (EC) was used as the electrolyte. Multiple coin cells were assembled in order to validate the reproducibility of the surface analysis and electrochemical experiments.

2.2. Imaging and Surface Analysis Characterization. Powder X-ray diffraction (XRD) measurements were carried out using a Rigaku Ultima III X-ray diffractometer (Cu Kα radiation, Rigaku, Japan), at an accelerating potential of 40 kV and a tube current of 20 mA, to identify the crystalline phase of the synthesized pristine powders and AlPO$_4$-coated powders before and after lithiation. XRD data were collected at 3’ min$^{-1}$ in the 2-theta range of 20–80°. Field emission scanning electron microscopy (FE-SEM, JSM-7500F, JEOL, Japan) was employed at working voltage of 15 kV to study the surface morphology of the prepared powders and cycled electrodes. Transmission electron microscopy (TEM, Carl Zeiss-LEO 922, Germany) at a working voltage of 200 kV and equipped with X-rays energy dispersive spectroscopy (EDXS) was used to determine the morphology and composition of...
the pristine and AlPO$_4$-coated samples. The samples were placed in a copper grid.

2.3. Electrochemical Characterization. Cyclic voltammetry (CV) tests were carried out at room temperature on a Series G-750 Potentiostat/Galvanostat/ZRA Gamry workstation in the potential window of 0.01–2.5 V versus Li/Li$^+$ at a scan rate of 0.2 mV s$^{-1}$. Galvanostatic charge and discharge capacity cycles were also carried out in this workstation at current densities of 50, 100, and 200 mA g$^{-1}$ between 0.01–2.5 V versus Li/Li$^+$ at room temperature. Electrochemical impedance spectroscopy (EIS) measurements were performed on a PARSTAT 2273 Potentiostat/Galvanostat (Advanced Measurement Tech. Inc.), with an applied AC signal amplitude of 5 mV peak-to-peak over a frequency range of 1 MHz to 10 mHz.

3. Results and Discussion

3.1. Imaging and Surface Analysis Characterization

3.1.1. Scanning Electron Microscopy (SEM). The morphology of the pristine and AlPO$_4$-coated MoO$_2$ electrodes, before and after cycling, is shown in Figure 1 in the scanning electron microscopy (SEM) images. Before cycling, the two powders were generally indistinguishable from one another. They have an average size of ~5 to 10 $\mu$m, indicating that the AlPO$_4$ coating did not lead to clumping or any other observable change in the microstructure of the anode particles. In comparison, cracks and crumbles are observed in the pristine material after cycling (Figure 1(c)) as a result of the large volume expansion during lithium insertion/extraction. This cracking and crumbling during cycling keeps generating new active surfaces that were previously passivated by the stable surface films [22]. Such cracks and crumbles are not observed (Figure 1(d)) in the AlPO$_4$-coated MoO$_2$ after cycling. It is quite likely that the AlPO$_4$ nanoparticle coating significantly reduces the formation of surface cracks induced by the volume expansion of the electrode material and therefore diminishes the repetitive formation of electrode/electrolyte interfaces affecting the capacity fading [22].

3.1.2. Transmission Electron Microscopy (TEM) and X-Ray Energy Dispersive Spectroscopy (XEDS). TEM images of pristine and AlPO$_4$-coated MoO$_2$ anode material were collected in order to determine the nature of the AlPO$_4$ coating nanoparticles. Figure 2(b) shows the core MoO$_2$ anode material uniformly covered by the AlPO$_4$ nanoparticles. Study
at higher magnification (Figure 2(c)) further reveals that the AlPO₄ nanoparticle coating consists of uniform particles with an average diameter of ~80 nm. The distribution of Al and P was examined by X-ray energy dispersive spectroscopy (XEDS) characterization technique and the results are displayed in Figure 3. EDS data confirm the presence of Al and P in the coating layer and the absence of Al or P components in the pristine sample. The presence of the Cu signal is due to the copper grid used in TEM analysis.

3.1.3. X-Ray Diffraction Analysis. The XRD patterns of pristine MoO₂ and AlPO₄-coated MoO₂ powders are shown in Figure 4. Figures 4(a) and 4(b) show the XRD patterns of the pristine and AlPO₄-coated MoO₂ powders before cycling, respectively. Both powders were confirmed to be well-defined monoclinic structure with the space group of P2₁/c, with no additional diffraction patterns related to AlPO₄ coating layer. Pristine and AlPO₄-coated powders showed the same lattice parameter values of \( a = 5.606 \) Å, \( b = 4.859 \) Å, and \( c = 5.537 \) Å (JCPDS card # 32-0671), revealing that the AlPO₄ coating was not incorporated into the anode material as no changes were perceived in the structure [23]. Furthermore, the two diffraction patterns overlap nearly identically, indicating that the sintering treatment or other procedures involved with the AlPO₄ coating did not result in distortion of the crystal lattice [5]. This result shows that the AlPO₄ is just coated on the surface of the MoO₂ powders [24]. Peaks between ~40–45° are characteristic of graphite [25], while the peaks at ~50° and ~74° correspond to the Cu-foil substrate (JCPDS card number 04-0836) [26]. As we want to evaluate if there are significant changes in
the lattice structure after cycling, lithium cells were opened inside and argon-filled glove box to recover the electrodes. These electrodes were rinsed in EC, dried under vacuum, and studied exposed by XRD. Figures 4(c) and 4(d) show the XRD data of the pristine and AlPO₄-coated MoO₂ samples after 50 cycles of galvanostatic charge and discharge. In the pristine sample (Figure 4(c)), a careful inspection reveals that diffraction peaks evolved in the 25°–35° 2theta range. This peak evolution, corresponding to Li₂O formation during lithiation process [27], may indicate a partial interchange of occupancy of Li⁺ and transition metal ions, giving rise to disordering in the lattice structure due to an irreversible loss of oxygen during cycling [28]. This interchange of occupancy is known to deteriorate the electrochemical performance of the layered material [29, 30]. Such peaks are not observed in the AlPO₄-coated sample (Figure 4(d)). This probably suggests that the evenly dispersed AlPO₄ coating suppresses microstructural defects and structural degradation, acting as a protective coating layer, and therefore enhancing structural stability of MoO₂ electrode material.

3.2. Electrochemical Characterization

3.2.1. Cyclic Voltammetry (CV) Studies. Cyclic voltammetry (CV) of pristine and AlPO₄-coated MoO₂ between 0.01–2.5 V at a scan rate of 0.2 mV s⁻¹ was performed at room temperature to understand the effect of AlPO₄ coating on the Li⁺ insertion/extraction behavior of MoO₂. Figure 5 shows two pairs of redox peaks at ~1.23/1.57 V versus Li/Li⁺ and ~1.50/1.80 V versus Li/Li⁺, corresponding to the reversible phase transition of LiₓMoO₂ and MoO₂ caused by the insertion and extraction of lithium ions [3, 31]. According to previous research [32, 33], the two reactions corresponding to the two redox processes observed in the cyclic voltammograms in Figure 5 are as follows:

\[
\text{MoO}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow \text{Mo} + 2\text{Li}_2\text{O} \quad (1)
\]

\[
\text{Mo} + x\text{Li}^+ + x\text{e}^- \rightarrow \text{Li}_x\text{MoO}_2 \quad (2)
\]

During discharge, the lithium bonds to the oxygen in MoO₂, forming Mo metal and Li₂O. Then, the Mo partially alloys/dealloys up to the theoretical limit of LiₓMoO₂ (~838 mAh·g⁻¹). For pristine MoO₂ (Figure 5(a)), oxidation peaks slightly shift to higher potentials while the reduction peaks slightly shift to lower potentials (indicated with arrows). In addition, as cycling proceeds, oxidation and reduction peak intensities decrease rapidly. This electrochemical behavior indicates the structural degradation of MoO₂ anode material and an increase in the internal resistance during cycling, leading to the fast capacity loss of the pristine MoO₂ anode material [24, 34]. Electrodes suffer from capacity loss and poor rate capability because there are incomplete reversible phase transition and local structural damages during lithiation. On the other hand, it is observed that the AlPO₄-coated MoO₂ (Figure 5(b)) shows better cycling stability compared to pristine MoO₂. During cycling, almost no oxidation and reduction peak shifts are observed, suggesting a more stable lattice structure. Furthermore, the peak intensity declines much slower than that of the pristine MoO₂, indicating that capacity retention is noticeably enhanced after the AlPO₄ nanoparticle coating.
3.2.2. Galvanostatic Charge and Discharge Capacity Studies.

To study the electrochemical performance of pristine and AlPO$_4$-coated MoO$_2$, charge and discharge capacities were measured at a potential window of 0.01–2.5 V at current densities of 50, 100, and 200 mA·g$^{-1}$ at room temperature. The first charge and discharge cycles for pristine and AlPO$_4$-coated MoO$_2$ electrodes, at a constant current density of 50 mA·g$^{-1}$, are represented in Figure 6. The first cycle charge capacity has been observed to be higher in the case of the AlPO$_4$-coated anode material (∼1008 mA·h·g$^{-1}$) compared to the pristine anode material (∼625 mA·h·g$^{-1}$). On the other hand, a higher first cycle discharge capacity is observed in the case of AlPO$_4$-coated MoO$_2$ (∼1015 mA·h·g$^{-1}$) compared to the pristine MoO$_2$ (∼650 mA·h·g$^{-1}$). These enhanced first cycle charge and discharge capacities can be attributed to the effective removal of lithium and oxygen from the host structure [35]. In both samples, there are two constant potential plateaus at ∼1.40 and 1.70 V on the first
charge cycles, as well as two potential plateaus at ~1.57 and 1.3 V on the first discharge cycles. These results are consistent with those reported by Liang et al. [33], since the inflection points between these potential plateaus represent a transition between monoclinic phase and orthorhombic phase in the partially Li$_{x}$MoO$_{2}$. It is clearly observed that surface modification with AlPO$_{4}$ nanoparticles can significantly improve the electrochemical performance of MoO$_{2}$ anode material. Pristine MoO$_{2}$ electrode shows an irreversible capacity (IRC) of 25 mAh·g$^{-1}$ during the first cycle, while the AlPO$_{4}$-coated MoO$_{2}$ electrode shows an irreversible capacity of 7 mAh·g$^{-1}$ during the first cycle. The observed IRC and initial discharge capacity values confirm that oxide ion vacancies are partially retained in the lattice during the initial charge. In other words, we can imply that surface modification suppresses the elimination of oxide ion vacancies. This could be attributed to the mechanism proposed by Armstrong et al. [36], suggesting that surface modification suppresses the elimination of oxygen vacancies during the initial charge and consequently allows a reversible insertion/extraction of higher amounts of lithium in the subsequent discharge cycles [36]. Figure 7 shows the initial charge and discharge profiles of the pristine and AlPO$_{4}$-coated MoO$_{2}$ anode materials at current densities of 50, 100, and 200 mA·g$^{-1}$. As shown in Figure 7(a), the initial discharge capacity of the pristine MoO$_{2}$ is 434 mAh·g$^{-1}$ at a current density of 100 mA·g$^{-1}$. When the current density is increased to 200 mA·g$^{-1}$, pristine MoO$_{2}$ only undergoes an initial discharge capacity of 219 mAh·g$^{-1}$. The pristine MoO$_{2}$ exhibits a relatively poor rate capability. Comparatively, the AlPO$_{4}$-coated MoO$_{2}$ exhibits an enhanced rate capability as illustrated in Figure 7(b). The discharge capacities of the AlPO$_{4}$-coated MoO$_{2}$ at current densities of 100 and 200 mA·g$^{-1}$ are 647 and 341 mAh·g$^{-1}$, respectively, indicating that the AlPO$_{4}$ nanoparticle coating significantly improves rate capability. The electrochemical data collected from the pristine and AlPO$_{4}$-coated MoO$_{2}$ electrodes are denoted in Table 1.

Now, let us compare the cycle performance of pristine and AlPO$_{4}$-coated MoO$_{2}$ electrodes considering the discharge capacity as a function of cycle number for the first 50 cycles, as presented in Figure 8. At a current density of 50 mA·g$^{-1}$, pristine MoO$_{2}$ exhibits an initial discharge capacity of 650 mAh·g$^{-1}$, as discussed above. It declines to 297 mAh·g$^{-1}$ after 50 cycles, with a capacity loss of 54%. By contrast, the AlPO$_{4}$-coated MoO$_{2}$ electrode delivers an initial discharge capacity of 1015 mAh·g$^{-1}$. It declines to 787 mAh·g$^{-1}$ after 50 cycles, with a capacity loss of 22%. Rate capability, cycling stability, and discharge capacities of the AlPO$_{4}$-coated samples are improved after 50 cycles compared to the pristine samples. However, with ongoing cycling, lithium ions can eventually penetrate the coating protective layer, thus becoming incorporated into the lattice of MoO$_{2}$. This can be ascribed to the gradual elimination of oxygen vacancies in the anode material, which can be part of the reason for the capacity fading during cycling. Generally, this improvement in the discharge capacity, rate capability, and cycling stability can be explained due to the obstruction of the transition metal ions by the AlPO$_{4}$ nanoparticle coating to migrate from the surface to the bulk in the vacant sites for the lithium insertion, therefore maintaining the high concentration of the available sites for lithium insertion [10]. The AlPO$_{4}$ coating is an electronic insulator, as reported by Kim et al. [22], indicating that most of the oxidation and reduction reactions with lithium ions and electrons occur mainly at the interface between the anode material and AlPO$_{4}$ coating and not at the interface of AlPO$_{4}$ coating and electrolyte. From these results, we conclude that AlPO$_{4}$-coated anode material holds better cycling performance compared to the pristine anode material.
Figure 8: Discharge capacity as a function of cycle number of pristine MoO$_2$ and AlPO$_4$-coated MoO$_2$.

Table 1: Electrochemical data of galvanostatic charge and discharge cycles for pristine and AlPO$_4$-coated MoO$_2$.

<table>
<thead>
<tr>
<th>Current density (mA g$^{-1}$)</th>
<th>Initial discharge capacity (mAh g$^{-1}$)</th>
<th>Pristine MoO$_2$</th>
<th>% Capacity loss after 50 cycles</th>
<th>Initial discharge capacity (mAh g$^{-1}$)</th>
<th>IRC (mAh g$^{-1}$)</th>
<th>% Capacity loss after 50 cycles</th>
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<tr>
<td>50</td>
<td>650</td>
<td>625</td>
<td>25</td>
<td>1015</td>
<td>201</td>
<td>341</td>
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<td>434</td>
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<td>677</td>
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<td>338</td>
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IRC: Initial Reduction Capacity
3.2.3. Electrochemical Impedance Spectroscopy (EIS). To better understand the reason for the enhanced electrochemical properties of the AlPO₄ nanoparticle coating, electrochemical impedance spectroscopy (EIS) was carried out for the pristine and AlPO₄-coated MoO₂ anode materials. The electrochemical impedance data were obtained after 3 cycles of galvanostatic charge and discharge at room temperature, since the solid electrolyte interface (SEI) film is formed during the first few cycles and changes very little during ongoing cycling [37]. EIS is an effective, nondestructive technique to understand the various phenomena occurring at the interface between the electrode and electrolyte. It is used to determine electrochemical cell impedance in response to a small AC signal at constant DC voltage over a broad frequency range, from MHz to mHz [38]. Impedance spectroscopy is a crucial parameter to determine the electrochemical performance of lithium ion batteries. With this characterization technique, different electrochemical processes occurring inside lithium ion batteries, such as charge transfer, double layer capacitance, and diffusion of ions in the electrode, can be studied by calculating the real and imaginary parts of the impedance. EIS measurements have been carried out on the lithium ion batteries to examine the electrochemical systems, involving interfacial processes and kinetics of electrode reactions, for the pristine MoO₂ and the AlPO₄-coated MoO₂. The results are shown in Figures 9(a) and 9(b), respectively, in the form of Nyquist plots. Determining the possible equivalent circuit, in order to interpret the data, is crucial in this electrochemical characterization technique [39]. The equivalent circuit used for fitting the impedance data is shown in Figure 10. From the Nyquist plots, it can be perceived that they are composed of two parts. The first one is a suppressed semicircle in the high-middle frequency region related to charge-transfer process, and the second one is an oblique straight line in the low frequency region representing typical Warburg impedance.

The suppression of the semicircle in the Nyquist plots is due to the overlap of two different semicircles. The appearance of two suppressed semicircles indicates the contribution of two different resistive elements to the total impedance of the electrochemical cell. This is observed generally in the impedance plot due to the combination of a capacitor element and a resistor element in parallel. The semicircle in the high frequency region corresponds to the resistance (Rₛ) due to the surface layer, or solid electrolyte interface (SEI) formation [40]. Capacity fading of the anode material during cycling is associated with the thickness of such layer on the anode particles. During cycling, the SEI layer grows thick due...
to the electrode/electrolyte reaction, thus deteriorating the electrochemical performance of the cell. Middle frequency semicircle corresponds to the charge transfer resistance ($R_{ct}$) across the interface and the low frequency oblique straight line arises due to the lithium ion diffusion in the bulk of the anode material [41]. The intercept value on the x-axis in the high frequency region corresponds to the resistance ($R_s$) due to the lithium ion conduction in the electrolyte [41]. Depression in the semicircle has been calculated by placing constant phase elements (CPEs) instead of pure capacitance, as shown in the equivalent circuit. Impedance parameters obtained after fitting the EIS experimental data are summarized in Table 2.

By analyzing the data we observed that the main influence to the impedance is from the charge transfer resistance ($R_{ct}$) and surface layer resistance ($R_s$). $R_s$ behavior has been observed to be similar in both samples. In the charged state, it is observed that the $R_{ct}$ value for the AlPO$_4$-coated MoO$_2$ is lower compared to that of the pristine MoO$_2$, and an increase in $R_{ct}$ is observed, respectively. This increase in the value of $R_{ct}$ is expected, due to the growth of the SEI layer at the electrode/electrolyte interface. In the case of the AlPO$_4$-coated sample, the decrease in the $R_{ct}$ value can be explained due to the fact that, during cycling, irreversible extraction of the oxygen and lithium occurs, creating vacancies in the crystal structure of the anode material and, therefore, leading to the decrease in the charge transfer resistance [42]. The decrease in $R_{ct}$ is helpful for improving the electron kinetics of the anode material, and, hence, enhancing the electrochemical performance of MoO$_2$ as anode material for lithium ion batteries [43]. On the other hand, in the discharged state, we observed that both $R_{ct}$ and $R_s$ from the AlPO$_4$-coated sample are relatively low compared to the pristine sample. Charge transfer process is considered to be a rate determining process, and the rate performance of the anode material particularly depends on the $R_{ct}$ [40]. AlPO$_4$ nanoparticles coating can support reducing the increase in charge transfer resistance, and, therefore, implying a better rate performance, compared to the pristine sample. These results are consistent with previous studies, indicating that charge transfer resistance decreases significantly with the incorporation of coatings [41, 44].

### 4. Conclusions

MoO$_2$ anode material has been successfully coated by AlPO$_4$ nanoparticles and the AlPO$_4$-coated electrode displays an enhancement in cycle-life performance. The AlPO$_4$ coating significantly reduces the formation of surface cracks induced by the volume expansion of MoO$_2$ anode material, diminishing the repetitive formation of electrode/electrolyte interfaces that affects the capacity fading. Electrochemical performance of pristine and AlPO$_4$-coated MoO$_2$ has been studied by galvanostatic charge and discharge, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS), in the voltage range of 0.01–2.5 V, indicating that the AlPO$_4$-coated MoO$_2$ exhibits enhanced rate capability and excellent cycle stability. Galvanostatic charge and discharge measurements, at a current density of 50 mA·g$^{-1}$, reveal that pristine MoO$_2$ exhibits an initial discharge capacity of 650 mAh·g$^{-1}$ and 54% capacity loss in 50 cycles, while the AlPO$_4$-coated MoO$_2$ exhibits an initial discharge capacity of 1015 mAh·g$^{-1}$ and only 22% capacity loss at 50 cycles. Cyclic voltammetry studies indicate that the improvement in cycling performance of the AlPO$_4$-coated MoO$_2$ that is attributed to the stabilization of the lattice structure due to the suppression of the elimination of oxygen vacancies from the anode material. Electrochemical impedance spectroscopy (EIS) shows that the AlPO$_4$ nanoparticle coating reduces the surface layer and charge transfer resistance. Surface modification with AlPO$_4$ nanoparticles is an effective way to improve the structural stability and electrochemical performance of MoO$_2$ as anode material for lithium ion batteries.

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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