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Boosting the electrochemical performance of spinel LiMn_2O_4 cathode material *via* copper surface decoration

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Abstract

The spinel LiMn_2O_4 (LMO) is a promising cathode material for lithium-ion batteries due to its low cost, abundance, relatively low toxicity, and straightforward processing. Despite these advantages, its practical application is hindered by capacity fading resulting from Jahn-Teller distortion and manganese dissolution. In this study, LMO was synthesized using the glycine-nitrate combustion method and subsequently surface-modified with metallic copper through electroless deposition. Characterization of the Cu-decorated LMO was conducted using X-ray diffraction, elemental analysis, scanning electron microscopy and X-ray photoelectron spectroscopy. Cyclic voltammetry indicated increased redox peak intensities and enhanced electrochemical reversibility, as evidenced by reduced peak-to-peak potential differences for LMO@Cu. At 0.1C, LMO@Cu achieved an initial discharge capacity of 114.3 mAh g⁻¹, surpassing the 103.8 mAh g⁻¹ observed for pristine LMO. Rate-capability assessments from 0.1C to 10C showed consistently higher discharge capacities for LMO@Cu, with the most significant improvement at 10C, where LMO@Cu and LMO delivered approximately 45 and 8 mAh g⁻¹, respectively. At 55 °C, LMO@Cu maintained 90.44 % capacity retention after 50 cycles, compared to 85.01 % for LMO. The improved performance is attributed to enhanced electronic transport and electrochemical kinetics facilitated by the dispersed copper phase.

Keywords

Lithium-ion batteries, lithium manganese oxide; surface metal modifier, capacity fading, charge-discharge

Introduction

The spinel LiMn_2O_4 (LMO) is a widely studied cathode material for lithium-ion batteries because of its low cost, abundance, environmental friendliness, and relatively high energy density. Despite these advantages, LMO suffers from capacity fading during repeated electrochemical cycling, which

limits its long-term practical application as a cathode active material in rechargeable lithium-ion batteries [1,2]. Various research groups have investigated and categorized the mechanisms underlying capacity degradation in lithium manganese oxide cathodes.

The tetragonal phase associated with the Jahn-Teller distortion can develop at the cathode surface at the end of discharge, primarily due to the presence of Mn^{3+} ions [3,4]. Electrochemical reactions between the cathode material and electrolyte can also occur at high potentials [3,5]. Repeated electrochemical cycling may reduce the crystallinity and structural stability of the cathode material [3,5]. Cation redistribution and positional disorder between Li and Mn sites have also been reported [3,5]. In addition, oxygen vacancies can develop within the crystal lattice, while the lithiated spinel structure may become thermodynamically unstable during cycling [3,5]. One of the most important degradation mechanisms is manganese dissolution, which is promoted by the disproportionation of Mn^{3+} and subsequent dissolution of Mn into the electrolyte, particularly in the presence of acidic species such as HF [3,5].

Extensive research has focused on mitigating capacity fading in LiMn_2O_4 (LMO) cathodes. Elemental doping, which involves partial substitution of Mn-site cations with appropriate dopants, has been investigated to enhance the structural stability and electrochemical performance of the spinel framework [6]. Concurrently, surface modification strategies, particularly oxide coatings, have been utilized as complementary methods to further stabilize LMO cathodes [7]. Despite these modifications, manganese dissolution and interfacial degradation may still occur, and the effectiveness of oxide coatings is influenced by their intrinsic properties and operational conditions [8]. Interfacial stabilization has also been examined in other lithium-battery systems [9], and transition-metal dissolution, along with its effect on electronic conductivity, has been documented for the related spinel cathode $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [10]. Additionally, capacity fading during cycling and degradation under elevated-temperature storage have been observed in LMO cathodes [11,12]. Collectively, these studies underscore the complementary roles of bulk structural modification and surface engineering in enhancing the electrochemical stability of LMO cathodes.

A variety of surface-modifying materials have been investigated for LMO cathodes, including ZnO [13], Al_2O_3 [14], ZrO_2 [15] and coatings of lithium borate and lithium borophosphate [16]. SiO_2 -coated LMO has also been assessed as an ion-sieve material for lithium-ion extraction from brine [17]. Other reported surface modifiers for LMO include CaCO_3 [18], Cr_2O_3 [19], Fe_2O_3 [20], $\text{TiO}_2(\text{B})$ [21], and lithium borosilicate (LBS) [22]. In a different cathode system, Ag/carbon double coating has been utilized to enhance the electrochemical performance of LiFePO_4 (LFP) cathodes [23]. These studies collectively indicate that surface modification can enhance interfacial protection, transport properties, or electrochemical performance, with the specific mechanisms and advantages depending on the material and application.

Among metallic surface modifiers, Ag has attracted particular attention for its high electrical conductivity and its ability to modify the cathode/electrolyte interface. Abbas *et al.* [24] demonstrated that Ag-modified LiMn_2O_4 exhibited lower Mn dissolution, reduced surface degradation, improved capacity retention (approximately 81.9 % after 60 cycles), and a lower capacity-fading rate of approximately 0.06 % *per* cycle. These improvements were associated with the high electronic conductivity of Ag and its beneficial influence on the electrode surface. Jiang *et al.* [25] also reported that nano-Ag modification enhanced the structural integrity of LMO during electrochemical cycling, particularly at high current densities. In addition to LMO, Ag-based surface modification has been investigated in other oxide cathode systems. Sun *et al.* [26] and Li *et al.* [27] reported that Ag-modified $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NCM811) exhibited improved capacity stability at high voltages (4.3 to 4.6 V), reduced microcrack formation, suppressed electrolyte oxidation and surface-film growth, and improved rate performance. Although these studies focus on NCM811 rather than LMO, they more

broadly demonstrate that conductive metallic surface modifiers can influence the cathode/electrolyte interface and improve the electrochemical stability of oxide cathodes.

However, the relatively high cost of noble metals such as Ag limits their attractiveness for large-scale applications. Copper (Cu) is an interesting alternative because it combines high electrical conductivity with substantially lower cost and is widely available for conventional electrode-processing technologies. In contrast to substitutional doping, using metallic Cu as a separate conductive phase on the surface of LMO particles offers the possibility of improving electronic transport without intentionally modifying the intrinsic spinel crystal lattice. In particular, discrete metallic Cu particles dispersed over the LMO surface can provide additional electronic pathways between neighboring active-material particles and may facilitate charge transfer throughout the electrode. Furthermore, the presence of Cu at the LMO surface may modify the local electrode/electrolyte interface and potentially influence the interfacial reactions associated with capacity fading.

Cu has previously been employed in several lithium-ion battery electrode systems. Chen *et al.* [28] demonstrated that a thin Cu layer on silicon nanowires improved electrical conductivity and effectively buffered the structural changes associated with cycling. Murugesan *et al.* [29] similarly reported that Cu modification of amorphous silicon particles improved electronic conductivity and particle integrity during electrochemical cycling. Wang *et al.* [30] developed a bicontinuous Cu/Li₄Ti₅O₁₂ scaffold in which Cu provided an efficient electronic pathway and contributed to high-rate lithium storage. However, these studies focus on Si and LTO anodes rather than LMO cathodes and therefore cannot be considered direct evidence of the electrochemical behavior of Cu-modified LMO. Instead, they provide general support for the ability of metallic Cu to enhance electronic transport in lithium-ion battery electrodes.

More directly relevant to oxide cathodes, Güler *et al.* [31] reported a Cu-modified LiCr_{2/3}V_{1/6}Mn_{1/6}O₂ cathode with improved specific discharge capacity and capacity retention. The improved electrochemical performance was attributed to the high electrical conductivity of Cu and its beneficial effect on the electrode/electrolyte interface, which resulted in reduced charge-transfer resistance and improved electrochemical kinetics. Nevertheless, LiCr_{2/3}V_{1/6}Mn_{1/6}O₂ is structurally and electrochemically different from spinel LiMn₂O₄. Therefore, the specific role of discrete metallic Cu particles dispersed over the surface of LMO particles remains insufficiently clarified.

In this context, the novelty of the present study lies in investigating metallic Cu as a distinct conductive surface phase on the spinel LiMn₂O₄, rather than as a substitutional dopant incorporated into the LMO crystal lattice or as a continuous coating layer. The discrete Cu particles distributed over the LMO surface are expected to provide additional electronic conduction pathways while preserving the intrinsic spinel structure of LMO. This approach also offers the potential to modify the electrode/electrolyte interface, thereby influencing the degradation processes responsible for capacity fading. Unlike previous studies on Cu in Si and LTO anodes, this work specifically investigates the effect of metallic Cu surface decoration on an LMO cathode and establishes relationships among Cu surface distribution, structural characteristics, specific discharge capacity, cycling stability, and rate capability. Thus, the study evaluates Cu as a relatively low-cost conductive surface modifier for improving the electrochemical performance of LMO while maintaining its characteristic spinel framework.

Experimental

Synthesis of spinel LiMn₂O₄

All reagents used in this study were of analytical-grade purity and required no further preparation. In the standard synthesis, stoichiometric amounts of LiNO₃ (Riedel-de Haën, Germany) and

$\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (Sigma, Germany) were dissolved separately in deionized water. Concentrated nitric acid (Merck, Germany) and glycine (Merck, Germany) were then added. Nitric acid matched the acetate anion content. The glycine-to-nitrate molar ratio was 1:4. Glycine served as fuel and a chelating agent. Nitrate and acetate ions provided oxygen for glycine burning. The solution was heated to a set temperature and stirred until the excess solvent evaporated. After solvent removal, a thick brown foam formed. With further heating, it ignited spontaneously, yielding a spongy, ash-like solid. This substance was pulverized and heated in a muffle furnace at 800 °C for 12 hours.

Preparation of Cu decorated LiMn_2O_4

0.78 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Merck, Germany) was dissolved in 10 mL of deionized water and 2.8 g of potassium sodium tartrate ($\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$, Merck, Germany) was subsequently added to this solution. Subsequently, a 1 M NaOH solution was introduced to the mixture until the pH reached 11.5 to 12.5. The solution was then filtered using blue band filter paper, and the final volume was adjusted to 60 mL with deionized water. After adding 0.5 g of LMO to the solution and thoroughly mixing, approximately 1 mL of formaldehyde solution (37 %, Merck, Germany) was slowly injected to promote copper reduction. The mixture was firmly sealed. It was permitted to rest overnight following agitation. The solid material acquired by filtering the mixture through a cellulose membrane filter using an ultrafiltration apparatus was subsequently rinsed with distilled water and dried in a vacuum oven at 100 °C for 12 h.

Characterization techniques

A Bruker, USA, D8 Advance X-ray diffractometer (XRD) with a graphite monochromator and $\text{Cu-K}\alpha$ radiation ($\alpha = 0.154 \text{ nm}$) was used to analyze crystal structures. Data were collected at 45 kV and 40 mA over a 2θ range of 10 to 90°, with 0.02° steps and 50 seconds *per* step. Rietveld refinement of XRD patterns was performed using HighScore 4.8.0 [32] to determine powder lattice parameters. Morphology was studied using Zeiss EVO, Germany, scanning electron microscopy (SEM) and Zeiss Gemini, Germany, 500 field emission scanning electron microscopy (FESEM) with energy-dispersive X-ray spectroscopy (EDX) to assess elemental composition. Copper content in the LMO@Cu cathode was quantified using a PerkinElmer, USA, AAnalyst 800 flame atomic absorption spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI 5000 VersaProbe, Physical Electronics, USA, spectrometer to investigate the surface chemical composition and elemental states of the LMO@Cu samples.

Electrochemical measurements

A lithium disk (11 mm diameter) formed from a 10 mm rod (Merck) served as the anode. The cathode was made with a slurry of 86 wt.% active material, 9 wt.% acetylene black and 5 wt.% PVDF binder in NMP. The slurry was applied to aluminum foil and dried overnight at 120 °C using a heated Dr. Blade coater (MTI Corp.). Discs were removed from the foil and pressed between two flat plates at 2 T cm^{-2} for 5 minutes. The discs were then dried under vacuum for 2 h at 120 °C and transferred to the glove box without exposure to air. The cathode electrodes were fabricated with a diameter of 12 mm, corresponding to a geometric area of approximately 1.13 cm^2 , an active material loading of 6 mg cm^{-2} (approximately 6.8 mg per electrode), and an average thickness of 75 μm .

Electrochemical tests were conducted using a Swagelok-type cell, built in an argon-filled glove box (Unilab, MBRAUN), with the produced powders as the positive electrode and metallic lithium discs as the negative electrode. The electrolyte was a 1 M LiPF_6 solution in a 50:50 weight ratio of ethylene carbonate (EC) and diethyl carbonate (DEC). A glass microfibre filter (Rnfilter No. 6) served as a separator.

All produced cells were stabilized for 6 hours before measurement. An eight-channel MTI battery analyzer was used to charge and discharge the batteries using galvanostatic methods. Electrode capacity was assessed *via* galvanostatic discharge-charge cycling on battery-testing equipment. This cycling was performed over 3.5 to 4.5 V at various current densities at room and elevated temperatures (55 °C). A VersaSTAT MC multi-channel potentiostat, galvanostat, and impedance analyzer were used to monitor cyclic voltammograms (CVs). CVs were measured at a scan rate of 0.1 mV s^{-1} from 3.25 to 4.40 V. A Swagelok three-electrode T-cell (USA) was used for electrochemical impedance spectroscopy (EIS) experiments. LMO and LMO@Cu were working electrodes. An 11 mm lithium disc and a lithium plate served as the counter and reference electrodes, respectively. A VersaSTAT MC multi-channel potentiostat/galvanostat/impedance analyzer performed EIS measurements with high accuracy and stability. EIS tests used an AC signal amplitude of 5 mV over 100 kHz to 50 mHz at a 3.6 V discharge state. The electronic conductivity of LMO and LMO@Cu was assessed by linear-scan voltammetry using the VersaSTAT MC multi-channel system.

Results and discussion

Figure 1a presents the XRD patterns of the synthesized pristine LMO and LMO@Cu cathode materials. Figure 1b illustrates the crystal structure of LMO.

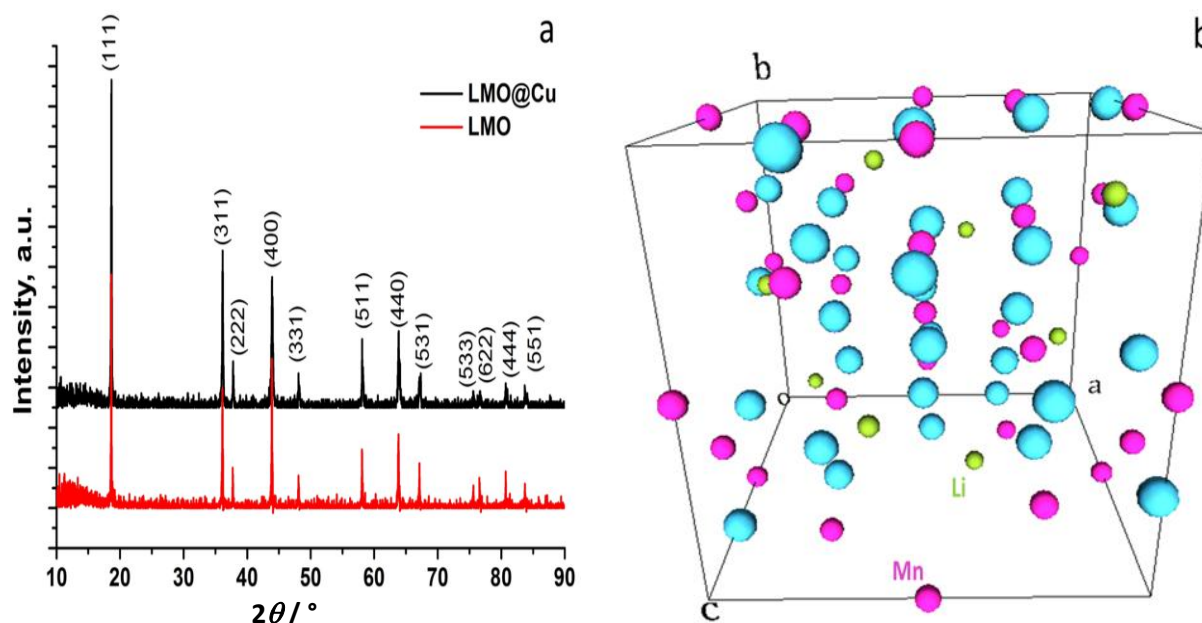


Figure 1. (a) X-ray diffraction patterns of LMO and LMO@Cu, (b) sketch of the crystal structure of LiMn_2O_4 (LMO)

The XRD patterns of the resultant material (Figure 1a) align with LiMn_2O_4 (JCPDS card No: 01-089-0118). The XRD powder pattern (Figure 1a) indicates that the LMO and LMO@Cu compounds are free of impurities and possess a cubic spinel structure characterized by the space group $\text{Fd}\bar{3}\text{m}$. The XRD patterns were analyzed and refined utilizing HighScore Plus software. The unit cell size parameters were determined to be $a = 0.82428(5) \text{ nm}$ for LMO and $a = 0.82418(6) \text{ nm}$ for LMO@Cu. The goodness-of-fit (GOF) parameters for the samples were 1.74145 for LMO and 1.74365 for LMO@Cu. The specified values are suitable for crystal phase analysis. The lattice parameters of both samples align with those reported in previous studies [33]. The distinctive copper peaks are absent from the XRD pattern because the amount of coated copper on the LMO is small. Atomic absorption spectrometry measurements indicate that the copper content in the LMO@Cu sample is 0.25 wt.%.

Figure 2 shows SEM images of the material's morphologies and microstructures. The uniform particle distribution of LMO and LMO@Cu materials is shown in Figures 2a and 2b. The particles joined together, as illustrated in Figures 2a and 2b, with the diameters of the LMO particles ranging from 100 to 200 nm.

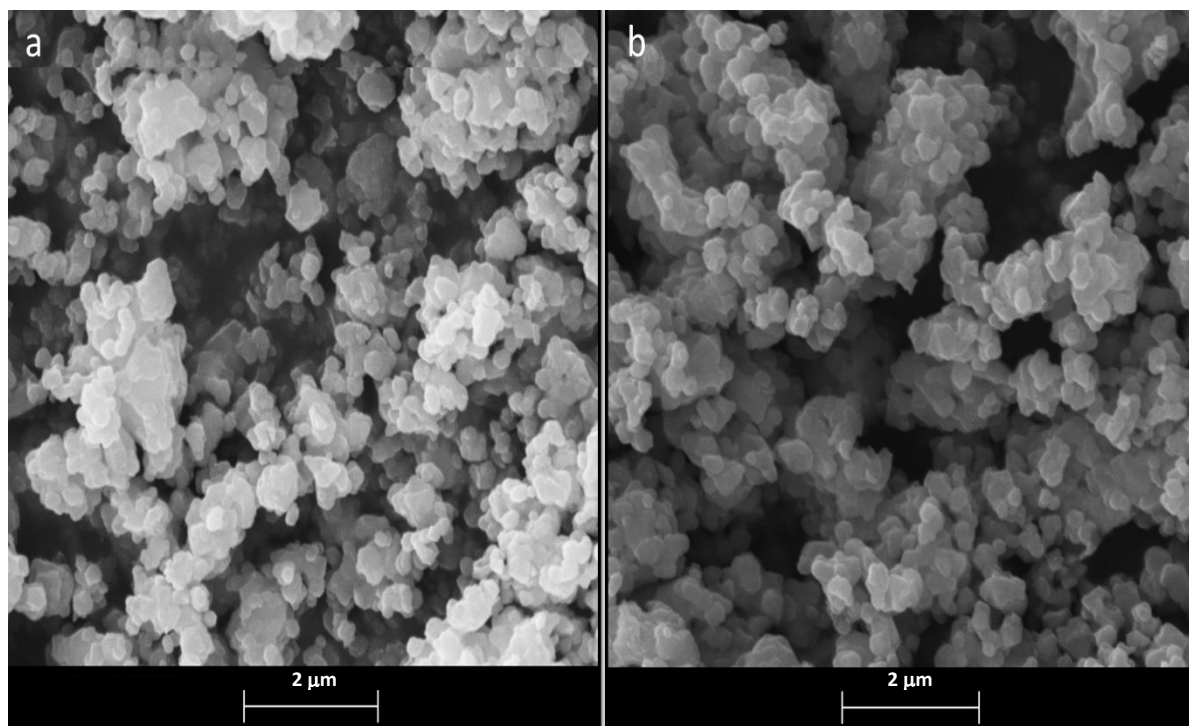


Figure 2. SEM micrographs of (a) LMO and (b) LMO@Cu

FESEM image, elemental mapping from EDX analysis and EDX spectrum of LMO@Cu are presented in Figure 3. The Cu element map analysis (Figure 3d) clearly shows that the LMO particle surfaces exhibit a uniform distribution of copper and that the particles are extensively coated with copper. Figure 3(e) displays the EDX spectrum of the Cu-coated LiMn_2O_4 sample. The EDX spectrum confirms the presence of oxygen (O), manganese (Mn) and copper (Cu) as constituent elements. The intense O and Mn peaks are attributed to the LiMn_2O_4 spinel structure, while the characteristic Cu L (~ 0.93 keV) and Cu $K\alpha/K\beta$ (~ 8.04 and 8.90 keV) peaks indicate successful copper incorporation. The relatively low intensity of the Cu peaks, compared to those of Mn and O, results from the limited amount of copper deposited on the particle surface. Because EDX detects X-rays from a large interaction volume, the LiMn_2O_4 substrate dominates the signal, and the thin copper surface decoration produces only weak characteristic peaks. Thus, the observed Cu signal supports the presence of a surface decoration rather than a bulk copper phase.

It has been determined that the LMO and LMO@Cu materials have electronic conductivities of 1.51 and $3.10 \mu\text{S cm}^{-1}$, respectively. The linear scan voltammetry measurement indicates that the electronic conductivity of LMO is doubled through Cu decoration.

The surface chemical composition of the LMO@Cu sample was analyzed using X-ray photoelectron spectroscopy (XPS) with a PHI 5000 VersaProbe spectrometer. Figure 4a-d presents the XPS spectra obtained from the LMO@Cu sample. The survey spectrum in Figure 4a displays characteristic signals of the LMO matrix along with distinct Cu-related signals. The primary Cu signals appear at approximately 932 to 933 and 952 to 953 eV, corresponding to the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ levels, respectively. Additional Cu-related signals are detected at approximately 87 to 88 eV (Cu $3s$), 74 to 75 eV (Cu $3p$), and within the Cu LMM Auger region. The O $1s$ signal is observed at approximately 529 to 531 eV,

while the C 1s signal at approximately 285 eV is mainly attributed to adventitious carbon from exposure to ambient air. The concurrent detection of multiple Cu photoelectron and Auger signals provides direct, surface-sensitive evidence for the presence of Cu within the XPS sampling depth.

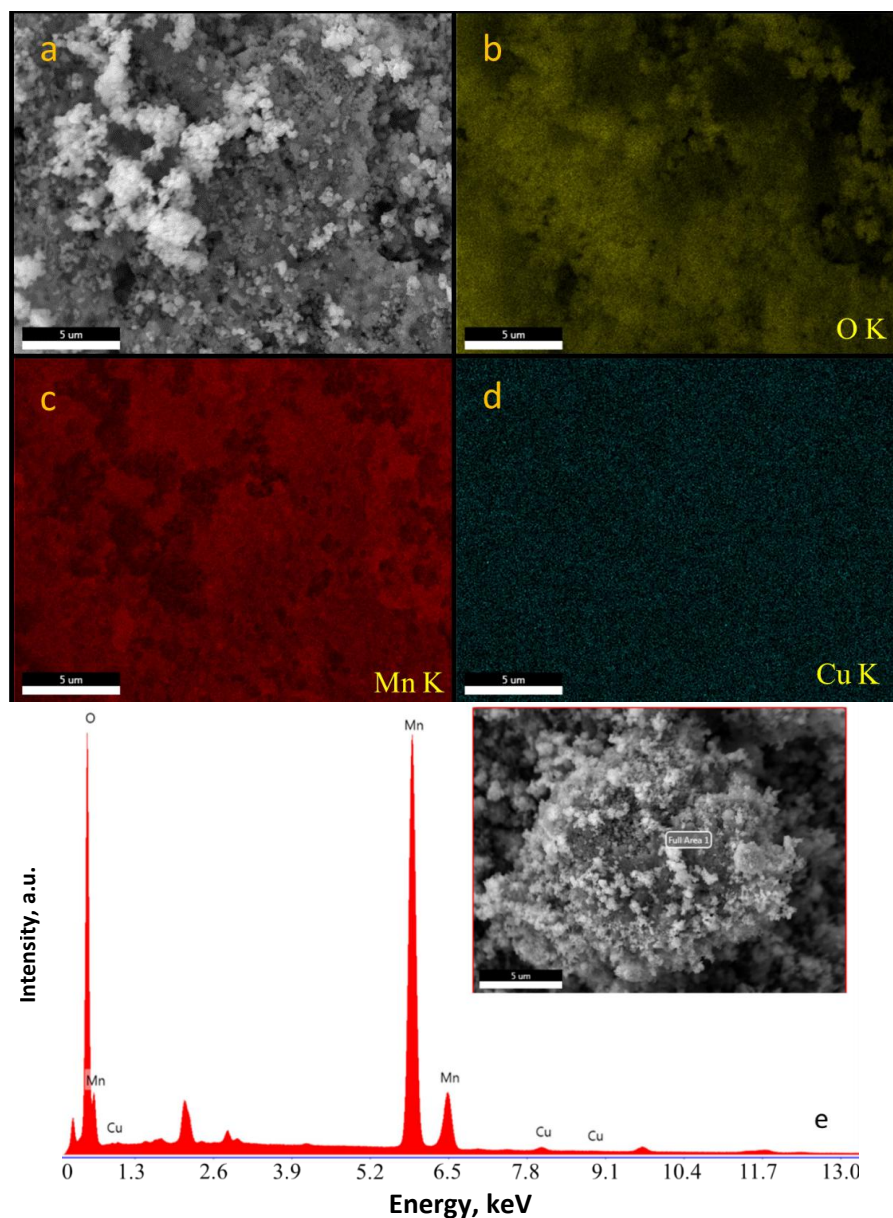


Figure 3. (a) FESEM image for mapping, elemental mapping of (b) O, (c) Mn, (d) Cu and (e) EDX spectrum of LMO@Cu

The expanded Cu 3s/Cu 3p and Mn 3p regions shown in Figure 4b further confirm the presence of Cu on the analyzed surface. The Cu 3s feature appears at approximately 87 to 88 eV, while the Cu 3p feature is observed at approximately 74 to 75 eV. The Mn 3p contribution is detected at approximately 53 to 54 eV. The detection of both Cu 3s and Cu 3p signals aligns with the Cu signals identified in the survey spectrum and confirms Cu presence within the surface-sensitive region of the LMO@Cu electrode.

The Cu LMM Auger region depicted in Figure 4c provides further insight into the chemical state of Cu. Cu LMM-related features are observed within the 540 to 570 eV binding-energy range. Notably, a pronounced Cu LMM feature is present at approximately 567 eV, with additional features at approximately 550 eV. Higher-binding-energy features in the 640 to 655 eV range are attributed to the Mn 2p region and overlap with Cu LMM-related transitions, as indicated in Figure 4c.

Given that the XPS measurements utilized an Al $K\alpha$ X-ray source ($h\nu = 1486.6$ eV), the Cu LMM feature observed at approximately 567 eV on the binding-energy scale corresponds to an Auger electron kinetic energy of approximately 920 eV. This value is indicative of Cu LMM Auger emission from low-valence or metallic Cu species, supporting the predominance of Cu^0 at the LMO surface. However, as high-resolution Cu 2p fitting and quantitative Auger-parameter analysis were not conducted, the relative proportions of Cu^0 and Cu^+ cannot be determined quantitatively. The XPS results support the presence of predominantly low-valence Cu species (Cu^0/Cu^+), while Cu^{2+} does not appear to be the dominant surface species. Partial oxidation of surface Cu^0 to Cu^+ cannot be excluded, as the Cu particles were exposed to the ambient atmosphere during sample handling and storage.

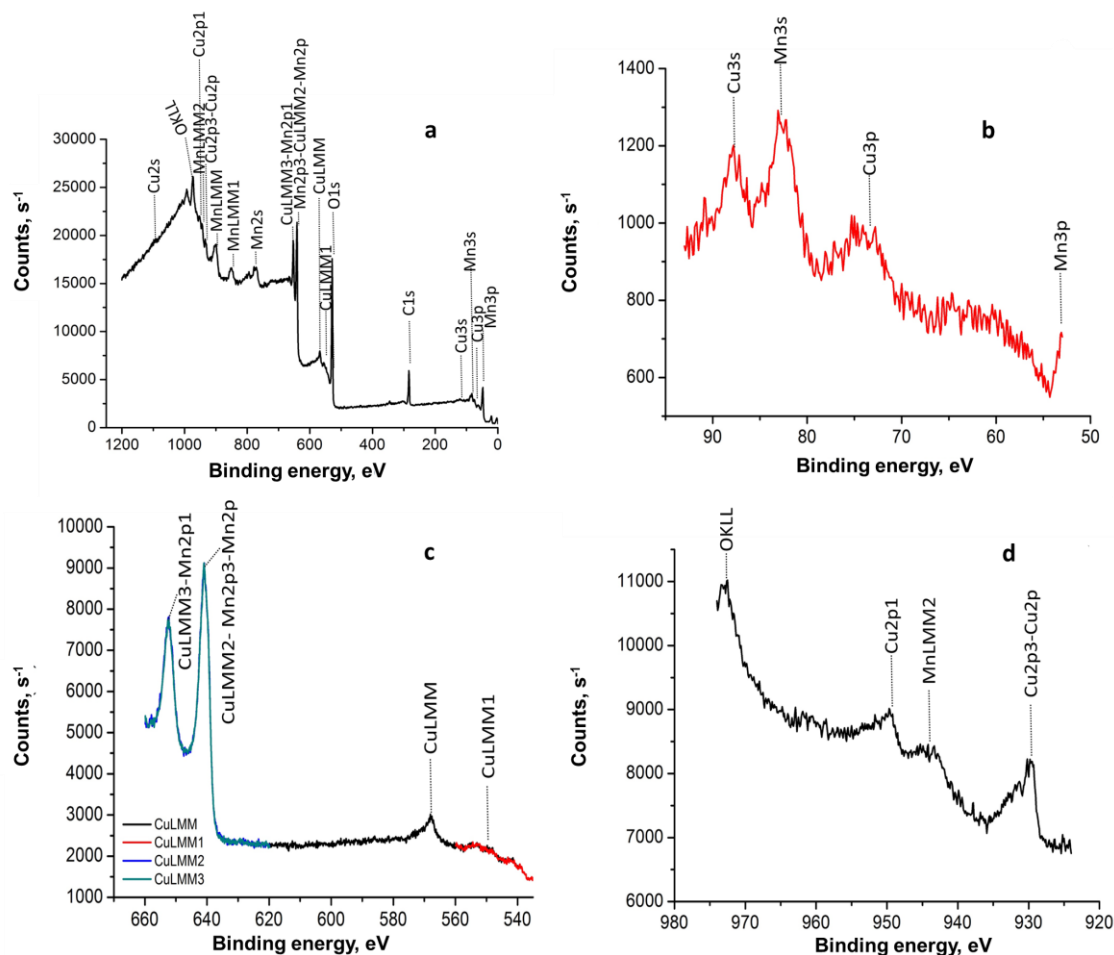


Figure 4. XPS spectra of the LMO@Cu sample: (a) survey spectrum, (b) high-resolution spectrum in the Cu 3s/Cu 3p and Mn 3p regions, (c) Cu LMM Auger spectrum, and (d) Cu 2p spectrum

The Cu 2p region shown in Figure 4d provides further evidence of Cu on the LMO surface. The $\text{Cu } 2p_{3/2}$ and $\text{Cu } 2p_{1/2}$ signals are centered at approximately 930 to 932 and 950 to 951 eV, respectively, resulting in a spin-orbit separation of approximately 20 eV, which is characteristic of Cu 2p photoemission. No pronounced satellite features indicative of a dominant Cu^{2+} species are observed in the Cu 2p spectrum. Thus, the Cu 2p spectrum aligns with the Cu LMM analysis and supports the conclusion that Cu^{2+} is not the predominant surface Cu species. The Cu present on the LMO surface is therefore considered predominantly low-valence or metallic Cu, although a minor contribution from surface-oxidized Cu^+ cannot be excluded.

Figures 5a and 5b present the cyclic voltammograms (CVs) of the LMO and LMO@Cu cathodes, respectively. Additionally, Figure 5c shows the CVs of both samples after the charge-discharge cycle.

The two distinct pairs of oxidation and reduction current peaks in LMO cathodes indicate a two-stage reversible phase transformation of the spinel LMO. Lithium ions are extracted from and reinserted into the spinel phase in a two-step process, as evidenced by two pairs of distinct redox peaks [34,35]. The CV tests indicate that Cu decoration improves the sharpness of anodic and cathodic peaks as well as the current density. After 50 cycles, the LMO@Cu electrode exhibits superior electrochemical reversibility compared with the pristine electrode under the same conditions.

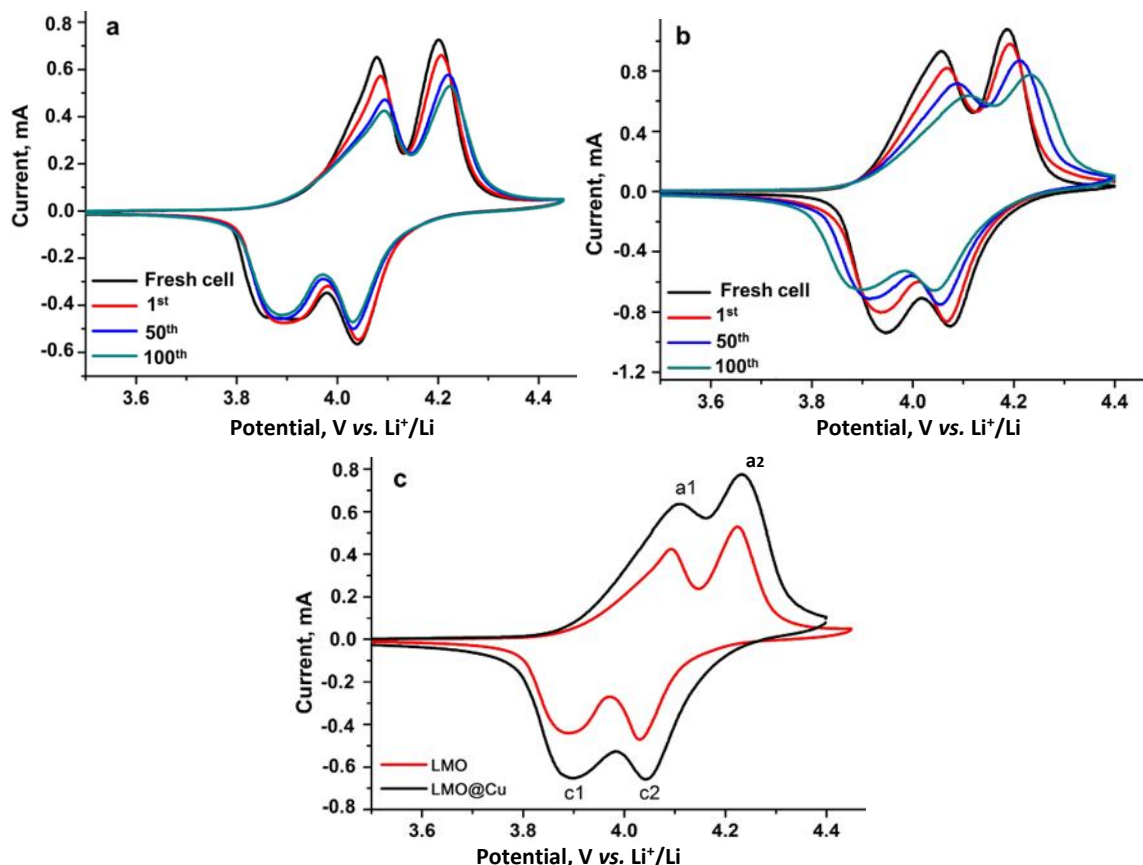


Figure 5. CV of (a) LMO, (b) LMO@Cu cathodes and (c) the comparison of the redox potential differences of the two electrodes after the 100th cycle

The Cu-modified electrode exhibits enhanced conductivity and kinetic properties, reflected in increased redox peak intensity and improved electrochemical reversibility. Enhancing electronic conductivity *via* the Cu decoration technique may alleviate electrochemical kinetic constraints on the LMO@Cu electrode. Table 1 displays the CV results for both electrodes.

Table 1. Values of the anodic (φ_{pa}) and cathodic (φ_{pc}) peak potentials and the corresponding potential differences ($\Delta\varphi_p$) for LMO and LMO@Cu electrodes

	LMO						LMO@Cu					
	φ_{pa1}/V	φ_{pa2}/V	φ_{pc1}/V	φ_{pc2}/V	$\Delta\varphi_{p1}/V$	$\Delta\varphi_{p2}/V$	φ_{pa1}/V	φ_{pa2}/V	φ_{pc1}/V	φ_{pc2}/V	$\Delta\varphi_{p1}/V$	$\Delta\varphi_{p2}/V$
Fresh cell	4.077	4.202	3.885	4.037	0.192	0.165	4.056	4.187	3.946	4.073	0.110	0.114
After 1 st charge-discharge	4.085	4.206	3.893	4.043	0.192	0.163	4.068	4.193	3.936	4.066	0.132	0.127
After 50 th charge-discharge	4.095	4.223	3.881	4.030	0.214	0.193	4.086	4.210	3.914	4.055	0.172	0.155

A larger potential gap between the anodic and cathodic peaks can increase electrode polarization, as illustrated in Table 1 and Figure 5. The LMO@Cu electrode exhibits lower $\Delta\varphi_{p1}$ and $\Delta\varphi_{p2}$ values (0.172 and 0.155 V, respectively) than the LMO electrode values of $\Delta\varphi_{p1}$ and $\Delta\varphi_{p2}$ (0.214 and 0.193 V, respectively). Modifications with Cu decoration may hinder the polarization of the active material.

Figure 6 illustrates the initial charge-discharge profiles for the LMO/Li and LMO@Cu/Li half cells at a 0.1 C rate. The charge/discharge curves of both electrodes exhibit two potential plateaus, consistent with the CV curves in Figures 5a, b, and c. The initial charge-discharge curves indicate that the Cu decoration process does not alter the electrochemical redox properties of the LMO cathode material [36]. The initial charge-discharge capacity of the LMO@Cu/Li half cell exceeds that of the LMO/Li half cell at the 0.1 C rate. Under identical charge-discharge conditions, the initial discharge capacity of LMO@Cu is 114.3 mAh g^{-1} , while that of the LMO electrode is 103.8 mAh g^{-1} . The improved discharge capacity of the LMO@Cu electrode can be attributed to reduced kinetic constraints in the electrode material, thereby enhancing electronic conductivity.

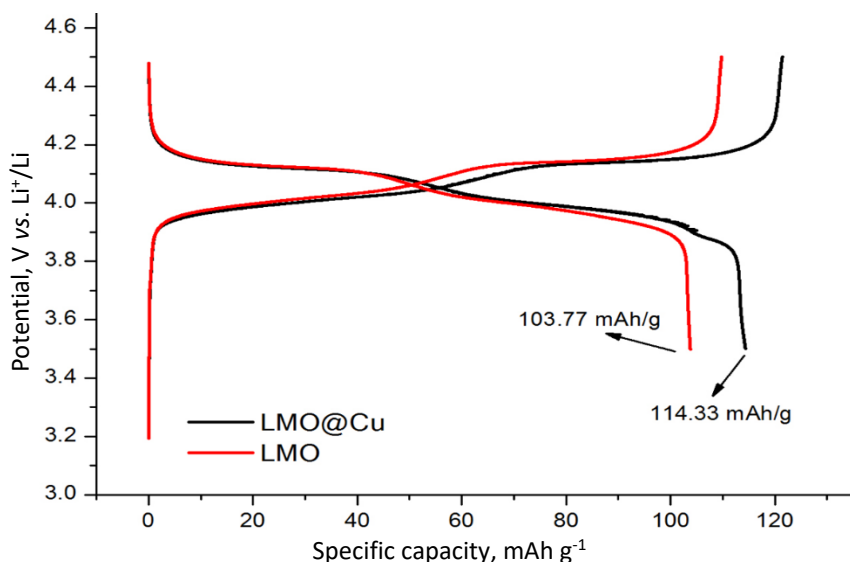


Figure 6. The charge-discharge voltage profiles of LMO and LMO@Cu at 0.1 C rate ($1 \text{ C} = 148 \text{ mA g}^{-1}$)

The specific discharge capacity values are presented in Table 2. Table 2 and Figure 7 clearly show that the specific discharge capacity of the LMO@Cu electrode exceeds that of the LMO electrode at all C rates. The difference in specific discharge capacity between the two cathodes increases at higher C rates, such as 5 C and 10 C. The increase in capacity of the Cu-coated cathode is attributed to the enhanced electronic conductivity of the cathode material and to accelerated lithium transport within the cell.

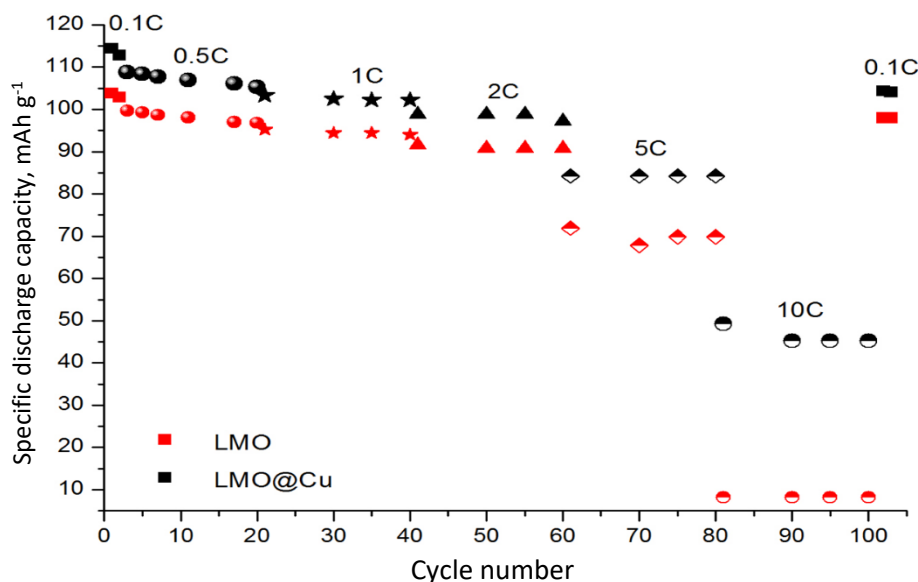


Figure 7. Discharge capacities of LMO and LMO@Cu electrodes at different current rates

Table 2. Charge-discharge performance of electrodes at various current densities

C-rate	0.1 C	0.5 C	1 C	2 C	5 C	10 C	0.1 C	
Charge-discharge cycle	1 st	2 nd	3 rd	21 st	41 st	61 st	81 st	102 nd
Discharge capacity, mAh g ⁻¹								
LMO	103.8	102.9	99.7	95.2	91.6	71.9	8.2	97.9
LMO@Cu	114.3	112.7	108.8	103.3	98.8	84.2	49.3	104.3

Figure 8 depicts the cycle performance of the LMO/Li and LMO@Cu/Li half cells. The cells underwent 100 charge-discharge cycles at C rates from 0.1 C to 10 C, followed by an additional 100 cycles at 1 C. Figure 8 shows that the 104th and 204th discharge capacities of the LMO electrode are 91.51 mAh g⁻¹ and 89.45 mAh g⁻¹, respectively, yielding a discharge capacity retention ratio of 97.75 %. The 104th and 204th discharge capacities of the LMO@Cu electrode are 99.63 and 91.09 mAh g⁻¹, respectively, providing a discharge capacity retention ratio of 91.42 %.

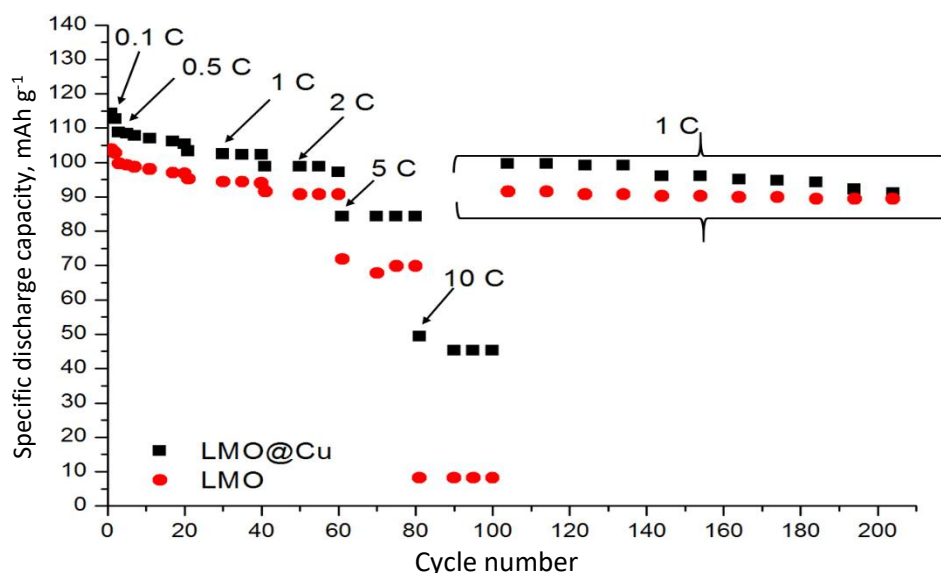


Figure 8. Cycling performance of LMO and LMO@Cu electrodes at a 1 C rate following 100 cycles conducted at 0.1, 0.5, 1, 2, 5 and 10 C rates, respectively

Figure 8 illustrates the rate capability of LMO and LMO@Cu electrodes across various current rates. The LMO@Cu electrode exhibits higher specific discharge capacities than pristine LMO, with the disparity becoming more pronounced at 10 C. At this elevated rate, LMO@Cu retains a discharge capacity of approximately 45 mAh g⁻¹, while pristine LMO achieves only about 8 mAh g⁻¹. This substantial enhancement under high-current conditions indicates that the surface-dispersed Cu phase introduces additional electronic conduction pathways and accelerates charge transfer, thereby increasing the utilization of the LMO active material at elevated rates.

The disparity between the two electrodes is less pronounced at 1 C, where the intrinsic reaction kinetics of LMO are sufficient for effective utilization of the active material, and the impact of additional Cu conductive pathways is minimized. When the current rate returns to 1C following high-rate measurements, both electrodes recover a significant portion of their discharge capacity. This observation suggests that the substantial capacity loss at high C-rates is primarily due to rate-dependent kinetic polarization rather than irreversible structural degradation. The superior high-rate performance of LMO@Cu indicates that the main benefit of Cu surface decoration is the enhancement of electronic transport and electrochemical kinetics, rather than the suppression of intrinsic degradation mechanisms in LMO.

Cycling performance of LiMn_2O_4 and $\text{LiMn}_2\text{O}_4@\text{Cu}$ electrodes at a 1 C rate at 55 °C

The cycle-life performance of both electrodes at 55 °C is shown in Figure 9. Both electrodes were charged and discharged 50 times at a 1 C rate. The initial specific discharge capacities of the Cu-decorated LMO and LMO electrodes were 103.30 and 109.82 mAh g^{-1} , respectively. After 50 cycles, the capacities were 93.43 mAh g^{-1} for the Cu-decorated LMO electrode and 93.37 mAh g^{-1} for the LMO electrode. The capacity retention of Cu-decorated LMO and LMO electrodes was 90.44 and 85.01 %, respectively. The cycling performance test at 55 °C demonstrates that a Cu decoration can enhance the LMO electrode performance.

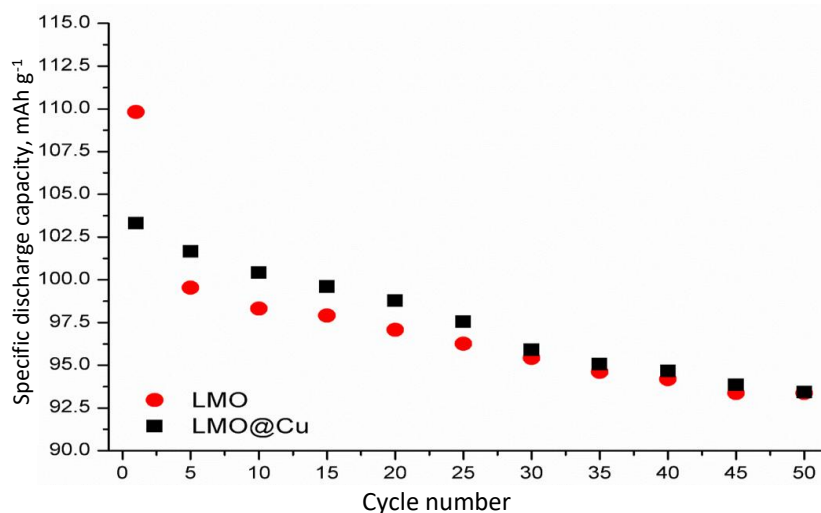


Figure 9. Cycling performance of LMO and LMO@Cu electrodes at a 1 C rate at 55 °C

The results indicate that Cu decoration on the LMO electrode improves the rate capability of the LMO cathode; however, it does not prevent capacity degradation. The decline in LMO cathode capacity is mostly attributed to LMO dissolution into the electrolyte, driven by disproportionation reactions and Jahn-Teller distortion. The Cu decoration may fail to enhance the structural stability of the LMO and may not serve as a protective barrier against the acidic electrolyte.

The electrochemical kinetic properties of the fabricated cathodes were evaluated using EIS. EIS measurements were performed initially on the newly constructed cell and subsequently after 50 cycles at room temperature (RT) and 50 cycles at 55 °C. (Figure 10 a, b, c).

The Nyquist plots show a slight intercept at high frequencies, a semicircle in the middle-to-high frequency range, and a linear extension in the low-frequency region. The spectra were examined by comparing them with the associated electrical circuit of the cell illustrated in Figure 10e. In this equivalent circuit, R_s represents the ohmic resistance of the electrolyte, while R_f , together with CPE1, describes the solid electrolyte interface (SEI) or surface film formed on the electrode. R_{ct} and CPE2 correspond to the charge-transfer resistance and the double-layer capacitance at the electrode-electrolyte interface, respectively, and capture the kinetics of the interfacial redox reaction. Finally, the Warburg element (W_o) reflects lithium-ion diffusion in the bulk electrode, indicating mass-transport limitations that dominate at low frequencies. Similar results have been noted by other research groups [37].

EIS experiments show that the R_s , R_f and R_{ct} values for the LMO@Cu electrode are lower than those for the LMO electrode. Furthermore, as shown in Figures 10a and 10b, the LMO@Cu electrodes of a fresh cell and a 50-times-cycled cell have lower total resistance than the LMO electrode. The EIS results demonstrate that Cu decoration can reduce the charge-transfer and SEI resistances of the LMO cathode.

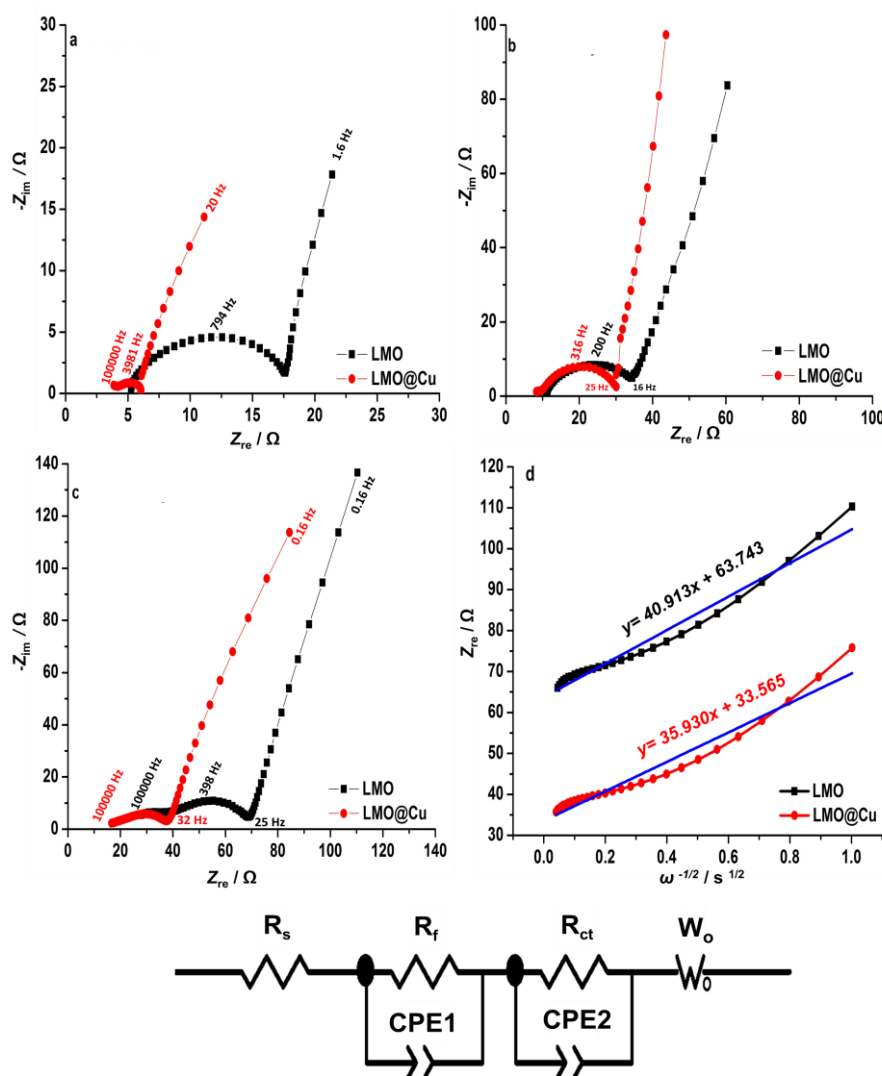


Figure 10. EIS patterns of electrodes (a) before cycling, (b) after the 50th cycle at RT and (c) after 50th cycling at 55° C, (d) the relationship between Z_{re} and $\omega^{-1/2}$ in the low-frequency region (e) equivalent electrical circuit of cells

Electrochemical impedance spectra were analyzed using the equivalent circuit $R_s(R_f||CPE1)-(R_{ct}||CPE2)-W_o$, which models electrolyte resistance (R_s), surface film resistance (R_f), charge-transfer resistance (R_{ct}), non-ideal capacitive behavior (CPE1 and CPE2) and lithium-ion diffusion *via* the Warburg element (W_o). The fitting quality is determined using ZView 4 equivalent-circuit modeling and impedance-analysis software and evaluated using the χ^2 criterion, yielding values of 5.02×10^{-4} for pristine LMO and 3.11×10^{-4} for the Cu-decorated electrode, demonstrating excellent agreement between experimental and simulated impedance spectra.

The fitting results indicate that Cu decoration substantially enhances interfacial electrochemical kinetics. The solution resistance decreased from 29.0 Ω for pristine LMO to 17.0 Ω after Cu decoration. Notably, the surface film resistance (R_f) decreased from 7.50 to 3.37 Ω , and the charge-transfer resistance (R_{ct}) decreased from 32.55 to 16.96 Ω , representing an approximately 48 % reduction. These findings suggest that Cu decoration promotes electron transport across the electrode/electrolyte interface and reduces interfacial polarization during cycling. Table 3 shows the equivalent circuit fitting parameters obtained from EIS spectra after the 50th cycle at 55 °C (Figure 10c).

Table 3. Equivalent circuit fitting parameters obtained from EIS spectra after the 50th cycle at 55 °C

Parameter*	LMO	LMO@Cu
R_s / Ω	29.00	17.00
R_f / Ω	7.50	3.37
$Q_1 / \mu\text{F s}^{(n-1)}$	0.118	1.38
n_1	1.144	1.043
R_{ct} / Ω	32.55	16.96
$Q_2 / \mu\text{F s}^{(n-1)}$	80.9	127
n_2	0.723	0.736
$\sigma / \Omega \text{ s}^{-1/2}$	40.913	35.930
χ^2	5.02×10^{-4}	3.11×10^{-4}

*CPE1 and CPE2 are constant phase elements used to account for the non-ideal capacitive behavior of the surface film and electrode/electrolyte interface, respectively. For a CPE, Q is the CPE coefficient, and n is the dimensionless exponent in $Z_{\text{CPE}} = 1/Q(j\omega)^n$, which describes the deviation from ideal capacitive behavior. χ^2 represents the reduced chi-square value indicating the goodness of fit.

Additionally, the reduced impedance values observed for the Cu-coated electrode align with its improved electrochemical performance and enhanced cycling stability at elevated temperatures. The decreases in both R_f and R_{ct} indicate that Cu decoration facilitates electron transport across the electrode/electrolyte interface, promoting faster charge-transfer reactions and lithium-ion transport during repeated charge-discharge cycles.

The lithium diffusion coefficients of two cathode materials are calculated from EIS data using Equation (1) [38-40].

$$D = \frac{R^2 T^2}{2A^2 n^4 F^4 C_{\text{Li}}^2 \sigma^2} \quad (1)$$

$R / \text{J mol}^{-1} \text{K}^{-1}$ and T / K denote the universal gas constant and absolute temperature, respectively. A / cm^2 represents the electrode's surface area, n indicates the number of electrons participating in the electrochemical reaction (1 for Li), F signifies the Faraday constant (C mol^{-1}), $\sigma / \Omega \text{ s}^{-1/2}$ denotes the Warburg impedance coefficient and C_{Li} refers to the Li-ion concentration within the material. C_{Li} is defined as the ratio of density to molar mass and was calculated *via* Equation (2) [41]:

$$C = \frac{1+1x}{180.81} 4.58 \quad (2)$$

In this equation, 180.81 (g mol^{-1}) represents the formula weight of LMO, and 4.58 (g cm^{-3}) is its density. Here, x denotes the stoichiometric amount of lithium inserted into LMO, which corresponds to the state of charge (%).

The Warburg impedance coefficient σ is associated with Z_{RE} by Equation (3):

$$Z_{\text{re}} = R_e + R_{ct} + \sigma \omega^{-1/2} \quad (3)$$

where ω is the angular frequency ($\omega = 2\pi f$).

Equation (3) was employed to define the correlation between Z_{RE} and $\omega^{-1/2}$ in the low-frequency domain, as demonstrated in Figure 10d. Following 50 cycles at 55 °C, the Li diffusion coefficients (D_{Li^+}) for LMO and LMO@Cu electrodes were calculated to be 8.71×10^{-15} and $1.13 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$, respectively. The data demonstrate that the LMO@Cu electrode has a higher lithium-ion diffusion coefficient than the LMO electrode. Thus, these experimental results indicate that the LMO@Cu electrode possesses commendable rate capability.

Conclusions

Glycine-nitrate combustion synthesis was employed to produce LMO cathode material, followed by successful electroless copper deposition during decoration. Scanning electron microscopy mapping confirmed that copper particles were uniformly coated onto LMO particles. Comparative

analysis revealed that the LMO@Cu electrode exhibited higher redox peak intensity and greater electrochemical reversibility than the pristine LMO electrode, as demonstrated by cyclic voltammetry testing. Electrochemical impedance spectroscopy studies showed that after 50 cycles at 55 °C, the lithium-ion diffusion coefficient (D_{Li^+}) of the LMO@Cu electrode reached $1.13 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$, compared to $8.71 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$ for the pristine LMO electrode. Continuous charge-discharge experiments at various C rates (0.1 to 10 C) indicated that the LMO@Cu electrode delivered a higher specific capacity than the LMO electrode. After 204 cycles at different current rates, the capacity retention for the LMO@Cu and LMO electrodes was 91.42 and 97.75 %, respectively. EIS measurements for half-cell polarization demonstrated that the solid electrolyte interphase resistance (R_f) and charge transfer resistance (R_{ct}) of the LMO@Cu electrode were lower than those of the LMO electrode. The copper-modified LMO cathode consistently exhibited a higher specific capacity than the pristine LMO cathode, as supported by electrochemical data. The improved specific capacity and cycling performance of the LMO@Cu cathode are attributed to enhanced electrochemical kinetics resulting from copper decoration. Copper particles increase electrical conductivity and facilitate lithium-ion migration during cycling. Consequently, the LMO@Cu cathode meets the requirements of lithium-ion batteries for improved high-rate performance at high C-rates, thanks to its enhanced electrochemical performance.

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