

Article

Electrochemical One-Step Synthesis of Cu₂O with Tunable Oxygen Defects and Their Electrochemical Performance in Li-Ion Batteries

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Abstract: We report a facile galvanic oxidation corrosion method for the preparation of cuprite nanocrystals (Cu₂O) with controllable oxygen vacancies. The Cu₂O microspheres have been employed as active anode materials in lithium-ion batteries (LIBs), exhibiting excellent electrochemical performance. The effect of oxygen vacancies on the electrochemical properties was studied. The oxygen vacancy-rich Cu₂O electrodes exhibited a high specific discharge capacity (1002.3 mAh g^{−1} at 0.1 C) and remarkable reversibility. Oxygen vacancies in Cu₂O not only promote high electronic conductivity but also provide additional active sites for lithiation/delithiation, further enhancing electrochemical performance. Furthermore, the formation mechanism of Cu₂O during the galvanic oxidation–corrosion process has been proposed.

Keywords: Cu₂O; oxygen vacancies; electrochemical synthesis; anode; lithium-ion battery



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1. Introduction

Lithium-ion batteries (LIBs) are widely used as electrochemical energy storage devices, but advancements in performance and cost reduction are crucial for significant progress in sectors such as electric vehicles and renewable energy storage [1–4]. The performance of these batteries primarily hinges on the characteristics of electrode materials, particularly anode materials, which have a direct impact on energy density, cycling stability, and rate capability [5–7]. Consequently, research has increasingly focused on developing anode materials with high specific energy, exceptional cycling stability, and environmental compatibility [8–10].

Cuprous oxide (Cu₂O), a typical transition metal oxide semiconductor, is considered as a promising anode material due to its high theoretical capacity, abundant resources, and eco-friendly properties [11–13]. However, like other metal oxides, Cu₂O is hindered by poor conductivity and cycling stability, which limit its potential as an anode material [14]. To overcome these challenges, various strategies have been employed, including particle size control [15,16], customization of microstructural morphology [17], and compositing Cu₂O with conductive materials [18,19]. Although many researchers have reported improvements in the electrochemical performance of Cu₂O through precise control of the particle size and morphology [20,21], these strategies alone cannot enhance cycling stability due to significant volume expansion and contraction during the charge and discharge processes [22].

To address these issues, researchers have proposed encapsulating nanoscale Cu_2O particles within porous carbon nanotubes [23] or forming nanosheet structures by compositing Cu_2O microspheres with graphene oxide [24]. These methods have been shown to effectively suppress the volume expansion of Cu_2O during the charge–discharge process, resulting in significant improvements in cycling stability. Experimental results have confirmed the effectiveness of these approaches. However, the relatively complex preparation processes and associated high costs present obstacles to large-scale batch production.

Remarkably, recent studies have shown that incorporating oxygen vacancies (OVs) into metal oxide electrodes serves as a cost-effective and efficient strategy to boost the electrochemical performance of lithium-ion batteries (LiBs) [25,26]. These oxygen vacancies not only modify but also optimize the electronic structure and microstructure of the electrodes, resulting in a substantial improvement in their conductivity [27,28]. Additionally, numerous studies have highlighted that oxygen vacancies in metal oxide anodes contribute to enhanced cycling stability and high reversibility in LiBs [29,30]. Dong [31] reported that introducing numerous oxygen vacancies into SnO_2 significantly enhances its electrical conductivity. The electrode, which comprises abundant oxygen vacancies in SnO_2 , refines its microstructure during charge–discharge cycles in LiBs, thus enhancing and stabilizing its capacity. Furthermore, He and colleagues [32] reported that Fe_3O_4 rich in oxygen vacancies, when used as an anode material for high-performance lithium-ion batteries, exhibits exceptional cycling stability and rate performance, achieving a reversible capacity of 921 mAh/g after 330 cycles.

Despite the promising potential offered by Cu_2O nanoparticles with tunable oxygen vacancies as anode materials for lithium-ion batteries (LIBs), there has been limited reporting on this topic. In this study, we introduce a novel electrochemical method for synthesizing Cu_2O nanoparticles with tunable oxygen vacancies. The experimental results indicate that the presence of oxygen vacancies significantly enhances the conductivity of Cu_2O and introduces additional active sites for ion intercalation and deintercalation, leading to a substantial improvement in its electrochemical performance. Additionally, our work provides insight into the formation mechanism of Cu_2O during the galvanic oxidation–corrosion process.

2. Experimental Section

2.1. The Synthesis of Cu_2O Nanoparticles with Oxygen Defects

Cu_2O nanoparticles, featuring oxygen vacancies, were synthesized in an electrochemical cell with a 100 g/L NaCl electrolyte solution, employing a copper sheet as the anode and a graphite plate as the cathode. A two-electrode system was used to synthesize Cu_2O nanoparticles with oxygen vacancies, using a copper sheet as the working electrode, a graphite sheet as the counter electrode, and a 100 g/L NaCl solution as the electrolyte. Asymmetric square-wave alternating current (AC) voltages were applied between the two electrodes, with positive voltages of +3 V, +6 V, and +9 V, and a negative voltage of −3 V. After 40 min of electrochemical reaction, brick-red suspensions were generated. The suspensions were then subjected to repeated filtration and washing to eliminate soluble impurities. The final products were dried in a vacuum oven at 60 °C for 8 h prior to further characterization. The nanoparticles synthesized at positive voltages of 3 V, 6 V, and 9 V are designated as Cu_2O -3, Cu_2O -6, and Cu_2O -9, respectively.

2.2. Characterization

The phase composition and crystalline structure of the synthesized samples were characterized by X-ray diffraction (XRD) with Cu $K\alpha$ radiation. The morphology and microstructure of the samples were examined using high-resolution transmission electron

microscopy (HRTEM). Additionally, the elemental composition and oxidation states were analyzed via X-ray photoelectron spectroscopy (XPS).

2.3. Electrochemical Measurements

CR2032 coin cells were fabricated to perform electrochemical tests on three distinct types of synthesized Cu_2O nanoparticles. A homogeneous slurry was uniformly dispersed using a mixture of the synthesized Cu_2O nanoparticles (80 wt%), acetylene black (10 wt%), and polyvinylidene fluoride (PVDF) binder (10 wt%) in N-methylpyrrolidone. The slurry was evenly coated onto copper foil and dried under vacuum conditions at 80 °C for 12 h. Thereafter, the coated foil was cut into circular electrode sheets, each with a diameter of 12 mm. The coin cells were assembled in an argon-filled glove box. These circular electrodes were used as the working electrode (anode), while lithium foil acted as the counter electrode. A polypropylene separator served as the separator, and a 1 M LiPF_6 solution in EC/DMC (1:1 volume ratio) was used as the electrolyte. Galvanostatic charge–discharge tests were performed using a NEWWARE battery test system, with the voltage ranging from 0.01 V to 3 V versus Li/Li^+ at room temperature. Additionally, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were conducted on a CHI660E electrochemical workstation. For the CV test, the voltage range was set from 0.01 V to 3 V, with a scan rate of 0.1 mV/s. The EIS measurements were conducted over a frequency range spanning from 0.01 Hz to 100 kHz.

3. Results and Discussion

3.1. Materials Characterization

The phase composition of the samples was determined by analyzing the X-ray diffraction (XRD) patterns illustrated in Figure 1a. The XRD patterns of the three samples exhibit distinct diffraction peaks at 2θ values of 29.582°, 36.441°, 42.328°, 61.406°, 73.556°, and 77.414°, which align with the (110), (111), (200), (220), (311), and (222) crystal planes of Cu_2O , as per JCPDS 78-2076 [33]. Notably, the distinct diffraction peaks at 2θ values are 35.504°, 38.735°, 48.66°, and 53.431°, which are attributed to CuO [34]. The intensity of CuO peaks increases with increasing the applied voltage. The Cu_2O -9 sample clearly indicates that, under conditions of applied high positive potential, Cu_2O may undergo additional oxidation to form CuO . Overall, the XRD results thereby confirm the success of the strategy used to synthesize Cu_2O nanoparticles by directly applying an asymmetric square-wave alternating current (AC) voltage to copper sheets.

X-ray photoelectron spectroscopy (XPS) was utilized to investigate the surface composition of the synthesized Cu_2O samples and to identify oxygen vacancies. As illustrated in Figure 1b, the signals corresponding to Cu, O, and C were clearly detected in the scanned XPS spectra of all three samples. The C signals detected in the three samples originate from carbon contamination [25]. The high-resolution scans of the O 1s XPS spectra (Figure 2c) and the Cu 2p XPS spectra (Figure 2d) further elucidate the valence states of the elements. Four clearly defined peaks are exhibited in Figure 2d, with their binding energies recorded at 934.30 eV, 942.50 eV, 954.10 eV, and 962.30 eV, respectively. The two peaks at 934.30 eV and 954.10 eV can be assigned to the binding energies of Cu 2p_{3/2} and Cu 2p_{1/2}, respectively; conversely, the peaks at 942.50 eV and 962.30 eV are attributed to the satellite peaks of Cu^{2+} [35]. Following the deconvolution of the Cu 2p_{3/2} and Cu 2p_{1/2} peaks, both peaks were resolved into two separate components to ascertain the chemical states of Cu. The peaks at 932.78 eV and 952.96 eV are attributed to Cu^+ , whereas those at 934.89 eV and 955.49 eV are ascribed to Cu^{2+} [36]. The presence of Cu^{2+} in the samples implies that CuO was generated during the electrochemical synthesis process, which is consistent with the XRD characterization results.

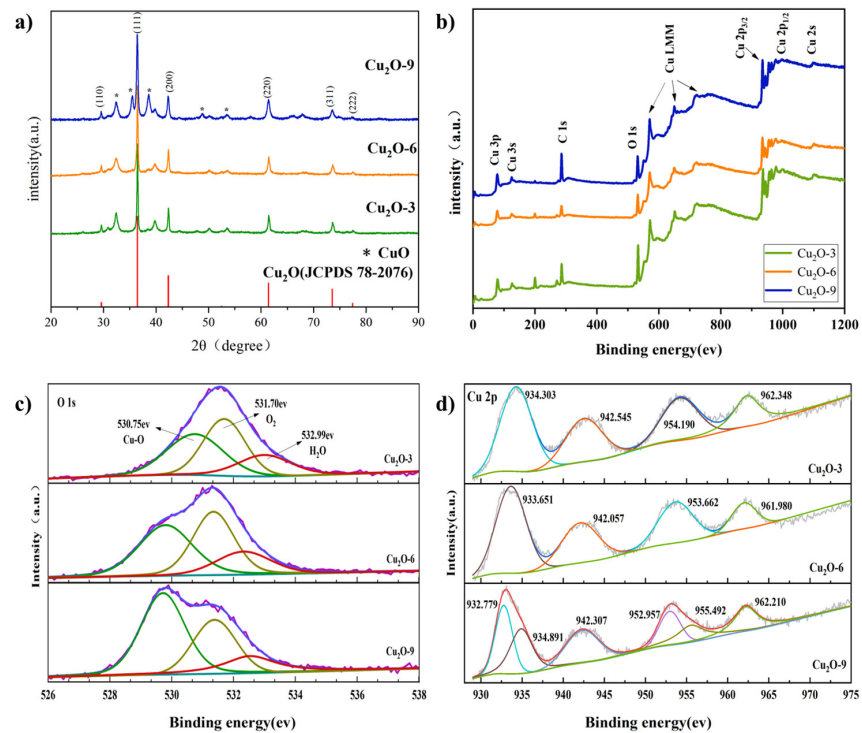


Figure 1. (a) XRD patterns, (b) XPS spectra, (c) O 1s XPS, and (d) Cu 2p spectra of samples Cu_2O -3, Cu_2O -6, and Cu_2O -9 samples.

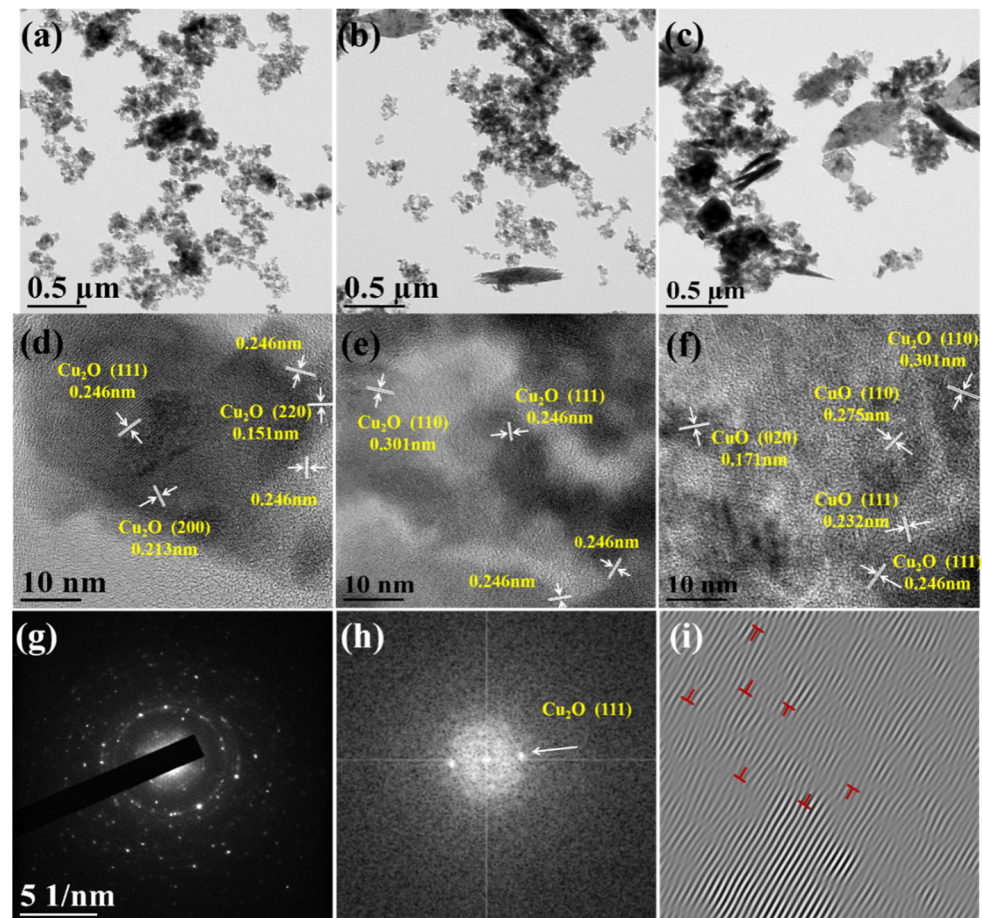


Figure 2. (a–c) TEM images and (d–f) HRTEM image of Cu_2O -3, Cu_2O -6, Cu_2O -9, (g) SAED pattern of the Cu_2O -6 sample, (h) FFT and (i) inverse FFT analysis of Cu_2O -6.

Similarly, the XPS spectra of the O 1s region can be fitted with distinct peaks centered at 530.75 eV, 531.70 eV, and 532.99 eV, assigned to lattice oxygen (Cu-O bond), oxygen vacancies, and adsorbed oxygen, respectively [37]. The relative peak areas indicate a systematic increase in the proportion of oxygen vacancies from the Cu₂O-3 to Cu₂O-9 samples. This observation implies that a higher applied positive potential during the electrochemical synthesis favors the generation of oxygen vacancies. XPS analysis revealed that the copper-to-oxygen atomic ratios for the samples, namely 0.58:1 (Cu₂O-3), 0.65:1 (Cu₂O-6), and 0.61:1 (Cu₂O-9), deviate significantly from the theoretical stoichiometric ratio of 2:1 for Cu₂O. This discrepancy can be ascribed to two factors: firstly, the presence of a substantial proportion of CuO in the synthesized samples; secondly, the contribution of oxygen vacancies, leading to adsorbed oxygen species, which account for the additional oxygen atoms. The XPS results further validate the existence of oxygen vacancies and provide insights into the impact of potential manipulation during the electrochemical synthesis on the Cu₂O samples.

Figure 2 illustrates the microscopic morphologies of the three synthesized Cu₂O samples. The particle size of Cu₂O gradually increases with an increase in the applied positive voltage during synthesis, as illustrated in Figure 2a–c. At a low positive voltage of 3 V, the Cu₂O-3 sample exhibits fine spherical particles with diameters of approximately 50 nm. When the voltage is increased to 6 V, the Cu₂O-6 sample displays irregular fusiform particles with lengths of approximately 400 nm and widths ranging from 100 to 200 nm. Upon further increasing the voltage to 9 V, the particle size increases significantly, and the particles adopt a more irregular shape. Morphological analyses of the samples synthesized at different voltages reveal that the applied voltage has a significant impact on both the morphology and particle size of Cu₂O.

The HRTEM images of the three samples, as depicted in Figure 2d–f, show distinct atomic lattice fringes. The measured lattice plane spacings of 0.246 nm, 0.301 nm, 0.213 nm, and 0.151 nm correspond to the (111), (110), (200), and (220) lattice planes of Cu₂O, respectively. The selected-area electron diffraction (SAED) pattern of the Cu₂O-6 sample, as shown in Figure 2g, further verifies the high crystallinity of Cu₂O. Additionally, lattice plane spacings of 0.171 nm, 0.232 nm, and 0.275 nm, corresponding to the (020), (111), and (110) crystal planes of CuO, were observed in the Cu₂O-9 sample, suggesting the presence of CuO. The HRTEM results are in agreement with the XRD findings, both of which confirm the formation of CuO in the Cu₂O-9 sample. Based on the XRD, morphological analyses, and HRTEM results, we conclude that high voltage facilitates the oxidation of Cu₂O, leading to the formation of CuO.

3.2. Electrochemical Investigation

Figure 3 presents the galvanostatic charge and discharge test curves of the Cu₂O sample assembled into a half-cell for this study. Figure 3a,c and e illustrate the voltage-capacity curves for the three battery groups during the first, second, and fiftieth charge-discharge cycles, respectively. The galvanostatic charge-discharge (GCD) curves of the three samples are at 0.1 C. The voltage-capacity curves of the three groups of batteries at the 1st, 2nd, and 50th charging and discharging cycles reveal initial discharging capacities of 569.9 mAh/g, 1002.3 mAh/g, and 823.8 mAh/g, respectively. It is noteworthy that the Cu₂O-6 group exhibits the highest initial charging (826.72 mAh/g) and discharging (1002.3 mAh/g) capacities. The first Coulomb efficiencies are 67.53%, 82.48%, and 75.62% for Cu₂O-3, Cu₂O-6, and Cu₂O-9, respectively. The results show that all three materials demonstrate relatively high initial discharge capacities; however, these materials exhibit significantly low first-cycle Coulombic efficiencies, indicating substantial capacity loss. The primary factors contributing to the low Coulombic efficiency observed in the first

cycle include irreversible reactions between Cu_2O and Li during the charge–discharge processes; and the formation of the solid electrolyte interface (SEI) layer resulting from the inevitable decomposition of the electrolyte [38,39]. During the subsequent cycles (from the second to the fiftieth), the Coulombic efficiencies remain stable at nearly 100%. After fifty cycles, the capacities of the three groups are 346.5 mAh/g, 453.6 mAh/g, and 461.4 mAh/g, respectively, representing retention rates of 80.32%, 66.25%, and 81.77%. It is noteworthy that, despite Cu_2O -6 exhibiting the highest initial capacity, its capacity decay is most pronounced after fifty cycles. When compared to previously reported Cu_2O nanoparticles, the Cu_2O samples with oxygen vacancies introduced through electrochemical methods demonstrate a significantly higher capacity retention ratio.

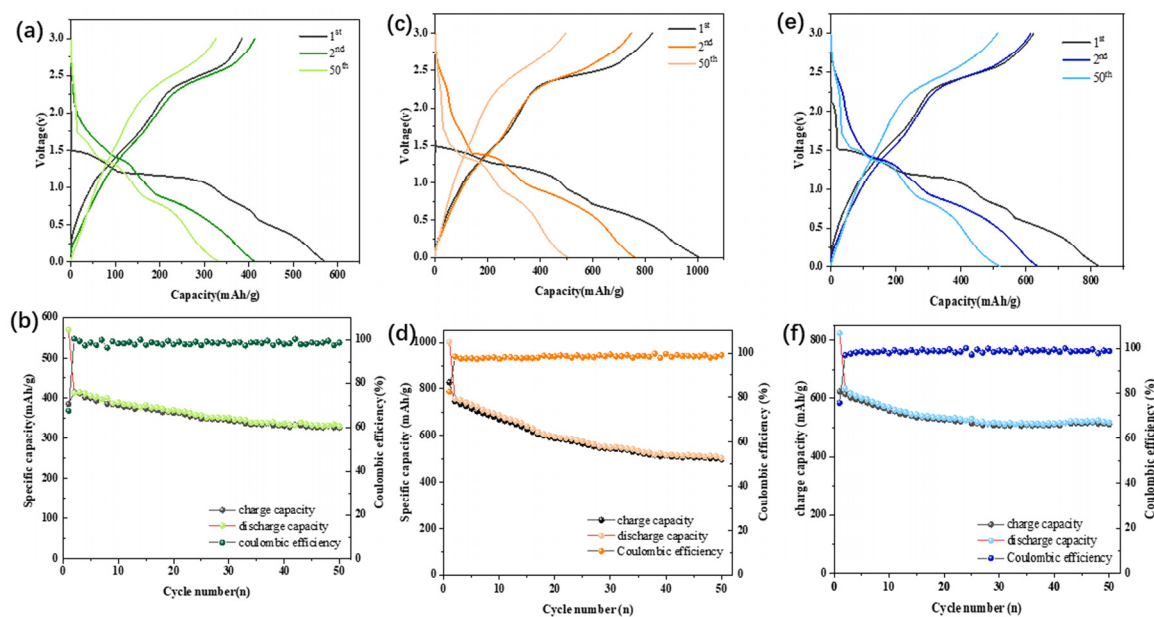


Figure 3. (a,c,e) Initial discharge–charge profiles, and (b,d,f) cycle performance of Cu_2O -3, Cu_2O -6, and Cu_2O -9 samples, respectively.

Figure 4 presents the rate performance of the three samples, which were cycled at current densities ranging from 0.1 C to 2 C, followed by a return to 0.1 C for an additional ten cycles. Specifically, the Cu_2O -6 sample exhibited discharge capacities of 631 mAh/g, 565 mAh/g, 493 mAh/g, 412 mAh/g, and 295 mAh/g at current densities of 0.1 C, 0.2 C, 0.5 C, 1 C, and 2 C, respectively. Upon returning to a current density of 0.1 C, the electrode maintained a relatively high discharge capacity of 527 mAh/g, which corresponds to 83.52% of its initial capacity. Similarly, the Cu_2O -3 and Cu_2O -9 samples also demonstrated excellent rate capabilities, with their capacities returning to 77.37% and 82.55% of their initial values, respectively. At a high current density of 2 C, the discharge capacities of Cu_2O -3, Cu_2O -6, and Cu_2O -9 were 296 mAh/g, 295 mAh/g, and 243 mAh/g, respectively, corresponding to 51.11%, 46.75%, and 45.59% of their respective initial capacities. These results demonstrate that cuprous oxide with oxygen vacancies maintains a relatively high capacity retention ratio under high current conditions. Notably, the Cu_2O -6 sample exhibited both the highest discharge capacity and the most favorable rate performance. However, the Cu_2O -6 sample experienced a relatively rapid capacity decay during high-current charge–discharge cycling, which is consistent with the results obtained from galvanostatic charge and discharge tests. Collectively, these rate test results reinforce the advantages of oxygen vacancy-rich cuprous oxide as an anode material for lithium-ion batteries, demonstrating its excellent kinetic performance.

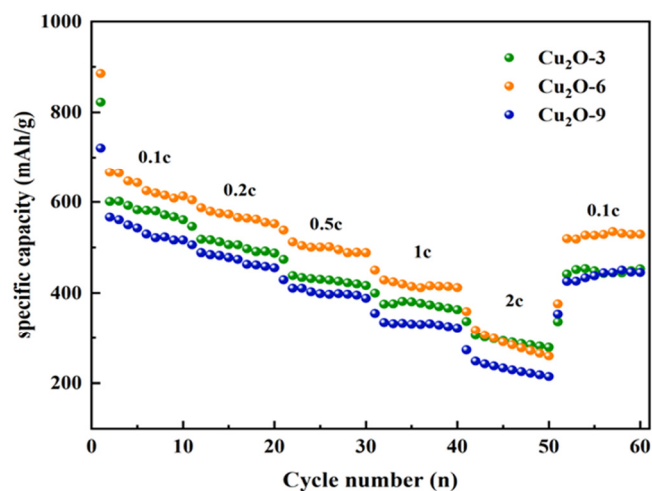


Figure 4. Rate performance of $\text{Cu}_2\text{O-3}$, $\text{Cu}_2\text{O-6}$, and $\text{Cu}_2\text{O-9}$ electrodes.

The kinetics of the electrochemical reactions within the battery were investigated using electrochemical impedance spectroscopy (EIS), with the resulting Nyquist plots displayed in Figure 5. The Nyquist plots of the three electrodes show a semicircle in the high-frequency range and a linear segment in the low-frequency range. The semicircle in the high-frequency range is representative of the charge transfer process related to the electrochemical reaction at the electrode's surface. Meanwhile, the linear segment in the low-frequency range signifies the diffusion process of ions moving from the solution to the electrode's surface [40]. An equivalent circuit model, illustrated in Figure 5, was used to fit the Nyquist plot. In this model, R_1 and R_2 represent the solution resistance and the charge transfer resistance (R_{ct}), respectively. CPE1 corresponds to the constant phase element arising from the double-layer capacitance between the solution and the electrode. W_1 represents the Warburg impedance, which relates to the diffusion resistance of ions within the solution [41]. The fitting results of the equivalent circuit indicate that the R_{ct} values for $\text{Cu}_2\text{O-3}$, $\text{Cu}_2\text{O-6}$, and $\text{Cu}_2\text{O-9}$ are $349.2 \, \Omega$, $584.2 \, \Omega$, and $596.9 \, \Omega$, respectively. It is noteworthy that the $\text{Cu}_2\text{O-3}$ sample exhibits the lowest R_{ct} value, potentially due to its smaller particle size (as suggested in [42]). These findings from the EIS analysis confirm the potential to improve the conductivity of cuprous oxide by introducing oxygen vacancies.

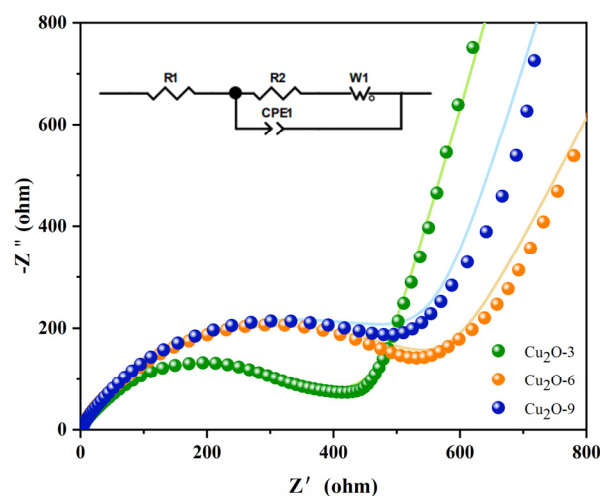


Figure 5. Electrochemical impedance spectra of $\text{Cu}_2\text{O-3}$, $\text{Cu}_2\text{O-6}$, and $\text{Cu}_2\text{O-9}$ electrodes.

To further investigate the influence of oxygen vacancies in Cu_2O on lithium-ion storage, cyclic voltammetry tests were performed, and the outcomes are depicted in Figure 6. In

the cyclic voltammetry (CV) profiles, all samples exhibited a prominent reduction peak within the voltage range of 0.7 V to 0.8 V. This peak is attributed to the formation of a solid electrolyte interphase (SEI) due to an irreversible reduction reaction between the electrolyte and Cu_2O [43]. Within the voltage range of 1.40 V to 1.68 V, faint oxidation peaks were observed, primarily linked to the decomposition of the SEI film. For Cu_2O -3 and Cu_2O -6, consistent oxidation peaks were visible in the range of 2.45 V to 2.62 V across all three cycles, attributed to the oxidation of copper to Cu_2O , as reported in previous lithium-ion battery cathode studies [11]. Conversely, for the Cu_2O -9 sample, an oxidation peak was noted within this potential range during the initial scan, but subsequent scans showed no significant oxidation peak. Analysis via X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) revealed the presence of some copper oxide in the sample, which may affect the lithium-ion storage mechanism.

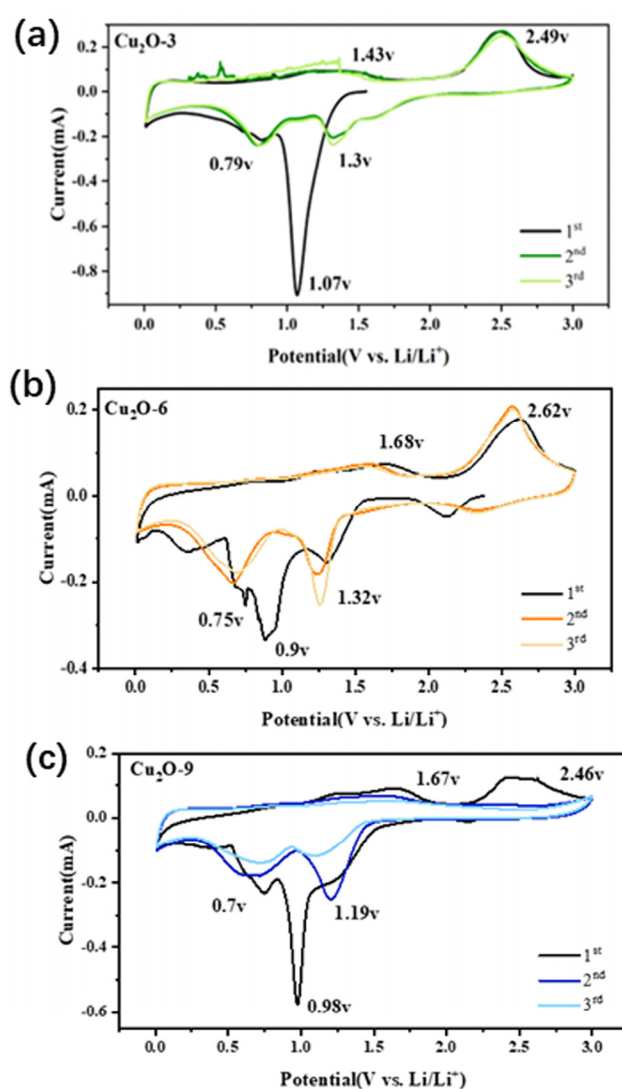


Figure 6. CV curves of the synthesized Cu_2O (a) Cu_2O -3, (b) Cu_2O -6, and (c) Cu_2O -9 electrodes.

3.3. Reaction Mechanism

A comprehensive investigation was conducted of the chemical composition, crystal structure, and electrochemical performance of Cu_2O enriched with oxygen vacancies. Based on the analysis, the synthesis process and formation mechanism of this Cu_2O variant were further explored, as depicted in Figure 7. Cu_2O can be synthesized through electrochemical reactions, with oxygen vacancies introduced by adjusting the applied voltages [44]. Specifically, during the positive voltage phase, the copper sheet functions as the anode,

undergoing oxidation to form Cu^{2+} . Simultaneously, the graphite electrode serves as the cathode, where H^+ ions, dissociated from water, are reduced to H_2 , leading to an increase in the solution's pH. Conversely, when negative voltages are applied, the copper sheet acts as the cathode and undergoes a reduction reaction, converting Cu^{2+} ions to Cu^+ [45]. Initially, a substantial amount of Cu^{2+} is produced, giving the solution a blue color. The high Cl^- concentration and low pH in the solution facilitate the complexation reaction between Cu^{2+} and Cl^- , forming $[\text{CuCl}_4]^{2-}$ and resulting in a gradual color change to light green. These experimental observations align with the preceding analytical results. Initially, the solution's color rapidly shifts from light blue to light green. As the electrochemical reaction proceeds, hydroxide ions accumulate, causing an increase in the solution's pH. Consequently, Cu^+ reacts with OH^- to form Cu_2O particles, which remain suspended in the solution and gradually turn it brick-red. During the negative scanning process, these Cu_2O particles further acquire electrons from the copper electrode, resulting in the formation of oxygen vacancies [46,47].

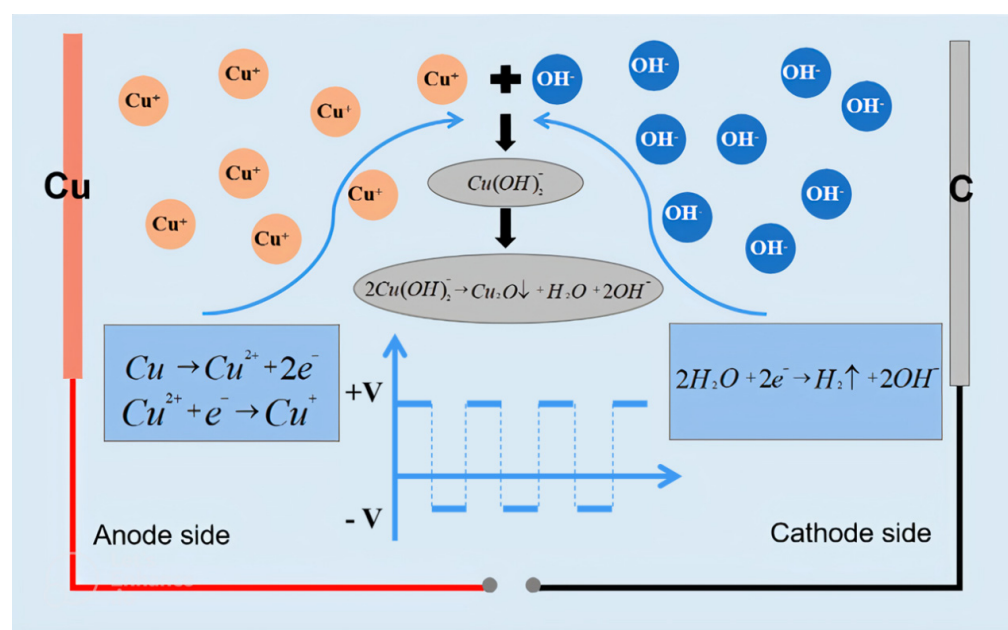


Figure 7. Schematic diagram of the electrochemical synthesis process of Cu_2O .

At a positive voltage of 3 V, the electrochemical reaction proceeds at a relatively slow rate, resulting in the formation of smaller cuprous oxide particles. This refinement leads to a substantial increase in the material's specific surface area, exposing more active sites for reactions and reducing the transmission distance for Li^+ and e^- . These factors collectively contribute to the lower charge transfer resistance observed in Cu_2O -3. As the positive voltage increases, the reaction rate at the electrode surface accelerates, leading to the rapid growth of Cu_2O particles. This rapid growth results in the formation of larger particles and the aggregation of smaller ones [48]. Furthermore, a portion of Cu_2O undergoes oxidation to form CuO , accounting for the presence of a certain amount of cupric oxide in the Cu_2O -9 sample.

4. Conclusions

In this study, we employed a versatile, cost-effective electrochemical process to synthesize Cu_2O nanoparticles with a tunable concentration of oxygen vacancies. Three samples were successfully synthesized using symmetric square-wave alternating current (AC) voltages, and the existence of oxygen vacancies in these samples was confirmed through X-ray photoelectron spectroscopy (XPS). These samples were subsequently utilized as anode

materials in lithium-ion batteries (LIBs), which demonstrated exceptional electrochemical performance. The presence of oxygen vacancies enhanced the conductivity and capacity of the LIBs, resulting in a high initial discharge capacity of 1002.3 mAh/g at a rate of 0.1 C, along with high reversibility. A mechanism for the electrochemical reaction of Cu₂O with oxygen vacancies was proposed, which is in agreement with our experimental results. The significance of this research lies in its introduction of oxygen vacancies (Ovs) into Cu₂O, thereby paving the way for new avenues of research in the field of lithium-ion batteries.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/coatings15050510/s1>.

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