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Urea-Assisted Sol-Gel Synthesis of LaMnO₃ Perovskite with Accelerated Catalytic Activity for Application in Zn-Air Battery

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Abstract: Precious metal-based materials such as commercial Pt/C are available electrocatalysts for redox reactions in Zn-air batteries. However, their commercial use is still limited by slow kinetics and restricted stability. In this work, we highlight a facial urea-assisted sol-gel method to synthesize A-site vacancy in LaMnO_{3+δ} oxide for boosting its catalytic activity and further explore the effect of the amount of urea on the A-site LaMnO₃. The A-site vacancy in LMO was confirmed by XRD, TEM, and XPS, which revealed that the urea-assisted sol-gel method mitigated the A-site vacancy in LaMnO_{3+δ} and increased its surface area, thus ultimately accelerating its redox reaction kinetics. The half-wave potential and current density of the resultant 3.0U-LMO electrocatalyst were 0.74 V and 5.74 mA cm⁻², respectively. It is worth noting that the assembled Zn-air battery with the 3.0U-LMO catalyst presented a power output of 130.04 mW cm⁻² at 0.51 V and a promising energy efficiency of 58.4% after 150 cycles. This protocol might offer an efficient approach for developing new defect-regulated perovskites for electrocatalysis.

Keywords: sol-gel method; Zn-air batteries; urea; redox reaction

1. Introduction

With today's excessive use of fossil fuels and the increase in environmental problems, the utilization of new energy storage and conversion technologies will certainly be an enduring research topic [1–4]. As a core energy storage technology, Zn-air batteries (ZABs) have attracted attention because of their good energy density and abundant reactive substances, especially the almost unrestricted oxygen used at the air electrode [5–7]. However, at present, the performance and stability of ZABs are dramatically hampered by their unsatisfactory high overpotential and slow kinetics of the redox reactions [8–10]. Up to now, precious metal-based materials such as Pt-based materials and IrO_2/RuO_2 are still considered to be the optimal candidates to remedy this situation [11,12]. However, high cost, low storage capacity, and poor durability greatly hinder the large-scale application of these materials in the air electrode of ZABs [13–16]. Therefore, it is greatly desirable to explore efficient and stable non-precious metal-based catalysts for the practical application of ZABs.

As one type of non-precious metal-based catalyst, perovskite oxides with a general formula of ABO₃ have become attractive due to their excellent oxygen reduction reaction (ORR) catalytic activity with earth-abundant precious metal-free elements [17,18]. They have been extensively studied for redox reactions in photocatalysis, electrocatalysis, and catalytic oxidation of some monoatomic oxides [19–22]. Among them, LaMnO_{3+ δ} (LMO) with an ideal eg filling of ~1 has been identified as an active catalyst for ORR [23]. However, the mass activity of bulk LMO towards ORR is only ~2 mA mg⁻¹, leading to poor efficiency in energy storage devices. To overcome this drawback, great research efforts have been



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). devoted to optimizing the catalytic activity of LMO oxide, among which several advanced synthesis approaches have been proposed [13]. For instance, Kim et al. synthesized LMO nanoparticles in a solution via laser ablation and reported that the mass activity was 20 times that of bulk LMO [24]. Xia et al. synthesized 3D-ordered LMO via a SiO₂ template method and demonstrated that the prepared LMO had better catalytic activity than LMO synthesized via a co-precipitation method [25]. Although these advanced synthesis techniques have improved the catalytic activity of LMO to some degree, they still face the problem of a complex and time-consuming synthesis process, and they are incapable of being mass produced.

Nowadays, the sol-gel method has been considered to be an efficient synthesis method to prepare perovskite oxide, as it can obtain a pure phase product and control its stoichiometry precisely [26–28]. To prepare LMO oxide via the sol-gel method, a mixture of cations is generally formed and then chelated with an organic complexing agent, to ensure that La³⁺ and Mn⁴⁺ are thoroughly mixed to an atomic level. Thus, the complexing agent plays a significant role in the phase structure, physical-chemical properties, and catalytic activity of LMO oxide [29]. An ethylene-diamine-tetraacetic acid (EDTA)-citric acid (CA) combination is commonly used to prepare LMO, as the combination of EDTA and CA can provide sufficient sites for the coordination of La³⁺ and Mn⁴⁺ ions and maintain full complexation [30]. However, the synthesized LMO sample with combined EDTA-CA as a complexing agent shows a low surface area after being sintered at a high temperature [31,32]. Additionally, surface segregation leads to inactive A-site cations surrounding the LMO surface. Thus, it is desirable to improve the sol-gel process to enhance the catalytic activity of LMO.

As a simple and low-lost organic compound, urea has been variously applied as a combustion agent and a precipitation agent. It has also been reported as a chelating agent in a $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ system. It has been demonstrated that the use of urea can offer superior advantages over the aforementioned EDTA-CA combination due to its low cost, excess yield, and low heat-treatment temperature [33,34]. Interestingly, Liu et al. indicated that the addition of urea is an effective means to generate A-site defects in perovskite for electrochemical energy storage [28]. Therefore, in this work, we further simplified the sol-gel synthesis process and used a one-step urea-assisted sol-gel method instead of EDTA to synthesize LMO perovskite. The effect of the amount of urea on the crystalline structure, ionic valence, microscopic morphology, and electrochemical performance of the synthesized LMO were investigated. In addition, we further studied the charge–discharge curves and the cycle performance of ZABs with the synthesized LMO as an air electrode.

2. Experiment

2.1. Synthesis Materials

The synthesis of LaMnO_{3+δ} (LMO) oxide via the urea-assisted sol-gel method can be described as follows. First, a certain amount of CA and urea were introduced to deionized water by continuous stirring, and ammonia was added to maintain the pH value at 8. Then, 0.1 mol manganese nitrate and 0.1 mol lanthanum nitrate were dissolved in deionized water under heating and agitation. Finally, the CA-urea solution was added into the metal ion solution. The obtained mixture was stirred and heated at 90 °C until it formed a yellow gel. The gel was dried overnight at 120 °C to obtain a spongy solid, which was then ground and sintered at 200 °C for 1 h. Then, the resulting precursor was further sintered at 750 °C for 2 h. The molar ratio of the urea to total metal ions was controlled to be 0, 1.5, 3.0, and 4.5, respectively, and the resulting products were denoted as xU-LMO (x = 0, 1.5, 3.0, and 4.5, respectively).

2.2. Preparation of Zn-Air Batteries

To prepare xU-LMO electrode ink for assembling ZABs, synthesized xU-LMO powder and commercial conductive carbon of equal weight were dispersed in a 5 wt.% Nafion solution and anhydrous ethanol and oscillated in an ultrasonic machine for 2 h. Here, we controlled the volume ratio of Nafion to anhydrous ethanol at 1:10. ZABs were fabricated with 6 M KOH as the electrolyte and 0.2 M zinc acetate and as the anode. Carbon cloth coated with xU-LMO electrode ink acted an air electrode. The final loading of xU-LMO on the electrode was 1 mg cm^{-2} .

2.3. Characterization

Crystalline structures of the synthesized xU-LMO oxides were determined using a Bruker D8 ADVANCE instrument. The morphology and microstructure of the xU-LMO samples were characterized using a Hitachi S-4800 scanning electron microscope. The specific surface areas were measured with an Autosorb-IQ3 system. Chemical composition and surface elemental states were investigated using an ESCALAB 250Xi X-ray photoelectron spectroscope. Thermal analysis (DTA and TG) was performed using a SDT Q600 thermal analyzer. The molecular structure was studied using a Nicolet 380 infrared spectrometer. The oxygen adsorption and desorption ability was characterized using a mass spectrum. The pretreating process referred to our previous work [14].

Electrocatalytic performances of the synthesized xU-LMO samples were characterized at room temperature in a standard three-electrode system with Ag/AgCl as a reference electrode, Pt as a counter electrode, and a catalyst coated on the polished glassy carbon as a working electrode. Here, 0.1 M KOH aqueous solution acted as the electrolyte. To perform electrochemical characterization, 5 μ L of the oscillated slurry was deposited on a polished glassy carbon electrode. The final specific surface load was 0.232 mg cm⁻². For comparison, commercial 20 wt%Pt/C (SPT-20, Suzhou Sinero Technology Co. LTD) was applied as a reference ink, and the loading was set as 0.116 mg cm⁻². Linear sweep voltammetry (LSV) curves were performed at variable rotational speeds (2000~400 rpm) to obtain stable cyclic voltammetry (CV) curves in the voltage range of 0.2~0.8. The electrochemical performance of the liquid ZABs was characterized by the LAND CT2001A battery test system at room temperature using a self-made zinc-air battery test device.

3. Results and Discussion

Thermal properties of the xU-LMO precursors with different amounts of urea were first investigated. As shown in Figure 1, a large amount of heat was released after introducing urea. As the amount of urea increased, exothermic peaks shifted towards higher temperatures. The TGA curve showed that a significant weight loss occurred at 200 °C, and the total weight loss at <500 °C was approximately 55% for a 0U-LMO precursor (Figure 1a). There were also two large exothermic peaks that appeared at 217 and 275 °C in the DTA curve. For a 1.5U-LMO precursor, abrupt weight loss was observed at 180 °C, followed by more weight loss at 260 °C. The total weight loss below 500 °C was approximately 90% (Figure 1b). Meanwhile, a significant exothermic peak at 254 °C and a small exothermic peak at 388 °C were observed in the DTA curve. In Figure 1c, a large exothermic peak at 238 °C and a broad one at 500 °C were observed for a 3.0U-LMO precursor in the DTA curve. The total weight loss <500 °C was approximately 78%. A 4.5U-LMO precursor presented two exothermic peaks at 271 and 437 °C. The total weight loss below 500 °C was approximately 75% (Figure 1d). Exothermic peaks at 200–300 °C in DTA curves referred to the reaction of CA with nitrates, and the exothermic peaks centered around 450 $^\circ$ C corresponded to the removal of nitrate and urea. Moreover, all precursors showed a minor exothermic peak at approximately 700 °C, indicating that the organics matter was basically decomposed, and the perovskite crystalline phase formed. Thus, the annealing temperature of xU-LMO precursors was set as 750 °C. However, it is worthwhile to mention that the adhesion between the precursor and the beaker was too strong to obtain enough 4.5U-LMO precursors, which suggested that excess urea should be avoided.



Figure 1. TGA/DTA curves of as-prepared (**a**) 0U-LMO, (**b**) 1.5U-LMO, (**c**) 3.0U-LMO, and (**d**) 4.5U-LMO precursors.

Figure 2 presents the XRD patterns of xU-LMO (x = 0, 1.5, 3.0, and 4.5) samples. The characteristic diffraction peaks of xU-LMO had a good correlation with the reported LaMnO_{3.15} perovskite structure, indicating the formation of a unique hexagonal symmetric perovskite phase. No other impurity peaks were observed except for the perovskite LMO, further proving that the urea-assisted sol-gel process was satisfactory. The 0U-LMO displayed a space group of Rc-3, which has been reported previously [16]. After introducing urea, it was observed that the main diffraction peaks of 1.5U-LMO, 3.0U-LMO, and 4.5U-LMO shifted slightly towards higher diffraction angles compared to 0U-LMO. Then, their XRD patterns were further analyzed by the Rietveld refinement method, with the obtained values displayed in Table 1. The addition of urea during the synthesis did not change their crystal structure significantly, and these samples still maintained the space group of Rc-3. However, the lattice parameter of 3.0U-LMO was larger than that of 4.5U-LMO, which is because 3.0U-LMO possessed a severer A-site deficiency than 4.5U-LMO (Table 1). This explains the above shift in the diffraction peaks as a result of the formation of A-site vacancy to maintain charge equilibrium. A possible reason for the generation of A-site vacancy is that NH⁴⁺ may partially occupy the A-sites of LMO in the urea-assisted sol-gel complexation process, since NH^{4+} has a similar ionic radius as La^{3+} . Then, NH^{4+} is removed via NH₃ formation during the subsequent high-temperature calcination, leaving behind A-site vacancy in LMO [28]. Meanwhile, the Mn⁴⁺/Mn³⁺ ratio for charge compensation also occurred with the A-site vacancy, which will be discussed later [16].

Table 1. The obtained values with Rietveld refinement method from XRD patterns.

Samples	Space Group	a	b	с	La-Site Occupy	Rw
1.5U-LMO	R-3c	5.5006 (3)	5.5006 (3)	13.3471 (4)	0.90908	13.26
3.0U-LMO	R-3c	5.5070 (8)	5.5070 (8)	13.3757 (8)	0.86238	14.65
4.5U-LMO	R-3c	5.5034 (9)	5.5034 (9)	13.3248 (3)	0.93393	13.33



Figure 2. (a) XRD patterns of xU-LMO (x = 0, 1.5, 3.0, and 4.5) perovskite oxides and (b) main peaks at around $2\theta = 32.5-32.7^{\circ}$ (data below the patterns are from JCPDS file with a number of 50-0298).

The morphology of as-synthesized xU-LMO samples was further characterized. As presented in Figure 3c,d, the synthesized xU-LMO sample with urea presented a sheet-like morphology with partial agglomeration. The reason may be that the addition of urea led to an increase in the alkalinity of the precursor solution during synthesis, resulting in the formation of particle agglomeration. To further verify the formation of A-site vacancy, 0U-LMO, 3.0U-LMO, and 4.5U-LMO perovskite materials were investigated with special aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM). It can be seen from Figure 3a-c that the lattice edges of 0U-LMO, 3.0U-LMO, and 4.5U-LMO were clear and regular, which illustrates that the introduction of urea during the preparation process did not cause significant changes in LMO phase structure. However, the interplanar lattice distances of 3.0U-LMO $(d_{110} = 0.268 \text{ nm})$ and 4.5U-LMO $(d_{110} = 0.264 \text{ nm})$ were smaller than that of 0U-LMO $(d_{110} = 0.274 \text{ nm})$, which also confirms that the urea influenced the symmetry of LMO perovskite and changed its crystalline surface spacing and parameters. Meanwhile, a partial absence of lattice fringes was also observed from the 3.0U-LMO and 4.5U-LMO samples, which is attributable to the generation of A-site cationic vacancies (circled in yellow). This result was consistent with the common belief that A-site defects affect the symmetry of the MnO_6 octahedron. Combined with XRD results, it was confirmed that the A-site vacancies were obtained in the xU-LMO sample. The elemental diagram in Figure 3d also clearly shows that the three elements of the synthesized 3U-LMO sample were distributed relatively uniformly. The specific surface areas of the 0U-LMO and 3.0U-LMO samples were measured to be 13.54 and 22.75 m² g⁻¹, respectively. This further indicates that the introduce of urea helped to improve the specific surface area of LMO, which is also consistent with the reported results [35].



Figure 3. (a–c) TEM images of LMO, 3.0U-LMO, and 4.5U-LMO; (d) SEM images and element mappings of 3.0U-LMO.

It is well known that the A-site vacancies, manganese ion valence state, and oxygen species attached to the LMO surface are determining factors of its ORR catalytic performance [16]. Thus, XPS analysis on synthesized xU-LMO samples was further performed. Figure 4a presents the overall XPS spectra of all samples with La 3d, Mn 2p, and O 1s peaks. As depicted in Figure 4b, the binding energies (BEs) of La $3d_{5/2}$ and La $3d_{3/2}$ were at 834.5 and 851.0 eV, respectively. Meanwhile, two satellite peaks at 838.5 and 855.4 eV appeared, indicating the electron transferred from O 2p to the empty orbit of La 5f. The spin-orbit splitting energy of the La 3d was about 16.6 eV, which is in good agreement with the reported pure La_2O_3 values by Ansari et al. [21]. So far, there has been an ongoing controversy about the catalytic activation of B-site cations in perovskites. Some researchers believe that their catalytic ability is related to the total content of variable valence ions at the B-site, because it provides suitable binding strength for the catalyst surface reactants or products. However, other researchers have affirmed that the higher valence state ratio of B-site cations is affiliated with catalytic oxidation reactions, because the high-valence ion has a weakening effect on the resistance to ion exchange compared with the low-valence state. It is understandable that these two statements have one thing in common, that is, the more ions in the higher valence state, the more favorable the catalytic oxidation reaction. As shown in Figure 4c, there are two peaks corresponding to Mn³⁺ and Mn⁴⁺ cations at 641.7 and 643.3 eV, respectively [36]. The surface molar ratio of Mn^{4+}/Mn^{3+} was further estimated. The order of the Mn^{4+}/Mn^{3+} ratio was 0U-LMO (0.85) < 4.5U-LMO (0.87) < 1.5U-LMO (0.91) < 3.0U-LMO (0.94). The relatively high proportion of the Mn⁴⁺ concentration in 3.0U-LMO might be due to the formation of A-site vacancy. In 0U- LMO oxide, La and Mn were linked by O atoms to form La-O-Mn. In 3.0U-LMO with A-site vacancy, the enhanced interaction between Mn and O resulted in an enhanced electron transfer to O and thus a rise in the valence state of Mn. In addition, according to Liu's analysis, the A-site vacancy also has consequences on

electronic modulation [21]. In Figure 4d, three oxygen counterparts corresponding to lattice oxygen (O_{latt}), surface-absorbed oxygen (O_{ads}), and oxygen-containing groups (O_w) are located at 529.1, 531.3, and 532.5 eV, respectively [37]. We further fitted the XPS data to the R_{Olatt} = O_{latt}/(O_{latt} +O_{ads}) value as the ratio of O_{latt} activated on the catalyst surface. The O_{latt}-activated content of different samples was ranked from smallest to largest: 0U-LMO (0.43) < 4.5U-LMO (0.47) < 1.5U-LMO (0.52) < 3.0U-LMO (0.54).



Figure 4. (a) XPS spectra, (b) La 3d levels, (c) Mn $2p_{1/2}$ levels, and (d) O 1s levels of xU-LMO (x = 0, 1.5, 3.0, and 4.5) samples.

To further evaluate the oxygen species, O₂-TPD was carried out on 0U-LMO, 3.0U-LMO, and 4.5U-LMO samples. The desorption peak appearing at T < 500 °C was commonly considered to be a weakly adsorbed oxygen species and/or active lattice oxygen near the surface (denoted as α -O₂), and the desorption peak (denoted as β -O₂) at T > 500 °C corresponded to lattice oxygen. As illustrated in Figure 5, compared to 0U-LMO oxide, the 3.0U-LMO showed an increased extent of the α -O₂ desorption peak and a downshift of the β -O₂ desorption peak, which is consistent with the previous XPS O 1s data. This result suggests that not only was the surface oxygen lattice in 3.0U-LMO activated, but the subsurface and bulk phase oxygen lattice was also activated to some extent. The results of both XPS and O₂-TPD suggest that the urea-assisted sol-gel method has a positive effect on increasing the lattice oxygen content of LMO, which is conducive to improving its catalytic ability.



Figure 5. O₂-TPD curves of LMO, 3.0U-LMO, and 4.5U-LMO oxides.

To evaluate the electrochemical catalytic activity of the synthesized xU-LMO perovskites, polarization curves at room temperature were obtained with a rotating ring-disk electrode (RRDE) in a 0.1 mol L^{-1} KOH solution containing saturated O₂. Figure 6a shows the cyclic voltammetry curves of all synthesized catalysts. Compared with 0U-LMO, the ORR performance of xU-LMO improved by adding urea. Among them, 3.0 U-LMO exhibited the highest peak voltage of 0.579 V, which also indicated that 3.0U-LMO had the strongest electrocatalytic ability. In addition, linear scanning voltammetry of the xU-LMO (x = 0, 1.5, 3.0, and 4.5) catalysts was investigated (Figure 6b). Specifically, the xU-LMO catalyst synthesized with urea exhibited more positive onset potential (E_{onset}) (0.87–0.92 V vs. RHE) than 0U-LMO (0.85 V vs. RHE). Moreover, a similar phenomenon can be found for the half-wave potential $(E_{1/2})$, with the value arranged in descending order as 0U-LMO (0.68 V) < 1.5U-LMO (0.70 V) < 4.5U-LMO (0.71V) < 3.0U-LMO (0.74V). The 3.0U-LMO catalyst exhibited the largest E_{onset} and $E_{1/2}$ and showed a similar potential value to the commercial Pt/C catalysts. In addition, 3.0U-LMO delivered a slightly higher limiting current density, with a value of 5.74 mA cm⁻². These results further confirm that the urea-assisted sol-gel method did improve the catalytic activity of LMO. Figure 6c shows the LSV curves of 3.0U-LMO at different rotational speeds. Similar to our reported studies, the number of electrons transferred (n) was also estimated from the slope of the K-L diagram [31,32]. The number of transferred electrons on the 3.0U-LMO catalyst was 3.94, 3.94, 3.95, and 3.91 at 0.35, 0.40, 0.45, and 0.50 V, respectively. Different from the reported combined 2- and 4-electron paths in 0U-LMO, 3.0U-LMO followed an almost 4e⁻ transfer process in alkaline electrolytes ($O_2 + 2H_2O + 4e^- = 4OH^-$). In addition, Tafel plots of 0U-LMO, 1.5U-LMO, 3.0U-LMO, and 4.5U-LMO were also compared. As shown in Figure 6d, 3.0U-LMO had the lowest slope, indicating that it had the lowest charge transfer resistance. To investigate the cycling stability, accelerated aging tests were performed on as-synthesized catalysts. The 0U-LMO and 3.0U-LMO catalyst slurries were subjected to 1000 consecutive potential cycles under the same test conditions to obtain new LSV curves. As can be seen from Figure 6e, f, the 3.0U-LMO maintained excellent perovskite stability, and the potential change ($\sim 20 \text{ mV}$) was much lower than the commercial Pt/C ($\sim 35 \text{ mV}$).



significant impact on the catalytic performance.

Figure 6. (a) CV curves and (b) LSV curves of xU-LMO (x = 0, 1.5, 3.0, and 4.5) catalysts, (c) LSV curves of 3.0U-LMO catalyst measured in the speed range 400–2000 rpm (inset: K-L plots for 3.0U-LMO catalyst at various potentials), (d) Tafel plots of xU-LMO (x = 0, 1.5, 3.0, and 4.5) catalysts, and LSV curves of (e) LMO and (f) 3.0U-LMO at 1600 rpm before and after 1000 consecutive cycles.

To assess the OER activity, LSV curves on xU-LMO samples were recorded in 0.1 M KOH solution, as presented in Figure 7a. As expected, xU-LMO with different amounts of urea delivered a more negative OER onset potential (E_{onset}) than the 0U-LMO without urea. For example, the E_{onset} of 0U-LMO, 1.5U-LMO, 3.0U-LMO, and 4.5U-LMO was 1.67, 1.64, 1.61, and 1.64 V, respectively. This performance improvement can be attributed to the generation of A-site vacancy on the LMO perovskite by the urea-assisted sol-gel process. Figure 7b shows the corresponding potential difference. The 3.0U-LMO presented a ΔE value of 0.99 V, which was the minimum value among the xU-LMO samples. Smaller ΔE values represent better bifunctional oxygen catalytic activity. These results further confirm the feasibility of preparing A-site vacancy perovskite oxides by the urea-assisted sol-gel method.

According to the above ORR and OER results, it is reasonable to consider that the 3.0U-LMO catalyst presented the best catalytic performance. Thus, the electrochemical performance of homemade ZABs with a 3.0U-LMO catalyst was further evaluated. As illustrated in Figure 8a, the peak power density of the 3.0U-LMO cathode reached 130.04 mW cm⁻² at 0.51 V, which is larger than commercial Pt/C (117.64 mW cm⁻²) and 0U-LMO (101.32 mW cm⁻²) [10]. As an air cathode catalyst with potential for ZABs, durability

was necessary for its practical application. As presented in Figure 8b-d, the ZAB with a Pt/C+RuO₂ electrode showed obvious voltage fluctuations after the charge–discharge cycle, whereas the one with a 3.0U-LMO catalyst remained stable even after 68 h. Notably, after 150 cycles of testing, the voltage efficiency of 3.0U-LMO was 58.4%, which was only a 1.1% decrease compared to the first cycle. These results illustrate that the 3.0U-LMO catalyst exhibits promising operational stability under a highly oxidizing electrolyte. In contrast, the voltage efficiency of the battery with the Pt/C+RuO₂ electrode decreased significantly after 150 cycles, demonstrating that the cycle durability of the 3.0U-LMO catalyst was more competitive. Experimental results in this study confirm that the 3.0U-LMO catalyst prepared by the urea-assisted sol-gel method was more competitive in catalytic activity and stability than pristine LaMnO₃, suggesting that the urea-assisted sol-gel method has a promising future for the preparation of air electrodes for rechargeable ZABs.



Figure 7. (a) OER properties over xU-LMO (x = 0, 1.5, 3.0, and 4.5) catalysts in 0.1 M KOH solution and (b) the potential difference (ΔE) between $E_j = 1$ mA cm⁻² (OER) and $E_{1/2}$ (ORR) of xU-LMO (x = 0, 1.5, 3.0, and 4.5) catalysts.



Figure 8. (a) *I-V* curves of the rechargeable ZABs with 0U-LMO, 3.0U-LMO, and Pt/C catalyst as the air electrode, respectively; (b) comparison of discharge–charge cycling features for 3.0U-LMO perovskite and Pt/C+RuO₂ at 10mA cm⁻²; the operation stability of ZABs with (c) 3.0U-LMO perovskite and (d) Pt/C+RuO₂ catalysts.

4. Conclusions

In conclusion, we have demonstrated a facile urea-assisted sol-gel method to enable the kinetics of LMO as an air electrode of ZABs. Further studies on synthesized xU-LMO have disclosed that the urea-assisted sol-gel method can introduce A-site vacancy into the LMO oxide, leading to a significantly accelerated catalytic activity of redox reactions. The amount of urea has a significant effect on the catalytical activity of xU-LMO oxides. The synthesized LMO with an optimal urea amount (3.0U-LMO) exhibited a maximum $E_{1/2}$ of ORR (0.74V) and a limiting current density (5.74 mA cm⁻²). In addition, a high voltammetric efficiency of 58.4% was still achieved after 150 charge/discharge cycles for assembled ZAB with the 3.0U-LMO air electrode, which was superior to that with commercial Pt/C and RuO₂. This study provides a facile and feasible strategy for designing perovskites with A-site vacancy as air electrodes for highly active ZABs.

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