Prevention of dendrite growth and volume expansion to give high-performance aprotic bimetallic Li-Na alloy-O₂ batteries

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Rechargeable aprotic alkali metal (Li or Na)- O_2 batteries are the subject of great interest because of their high theoretical specific energy. However, the growth of dendrites and cracks at the Li or Na anode, as well as their corrosive oxidation lead to poor cycling stability and safety issues. Understanding the mechanism and improving Li/Na-ion plating and stripping electrochemistry are therefore essential to realizing their technological potential. Here, we report how the use of a Li-Na alloy anode and an electrolyte additive realizes an aprotic bimetal Li-Na alloy- O_2 battery with improved cycling stability. Electrochemical investigations show that stripping and plating of Li and Na and the robust and flexible passivation film formed in situ (by 1,3-dioxolane additive reacting with the Li-Na alloy) suppress dendrite and buffer alloy anode volume expansion and thus prevent cracking, avoiding electrolyte consumption and ensuring high electron transport efficiency and continued electrochemical reactions.

urrent lithium ion (Li-ion) technologies, even when fully developed, have difficulty satisfying society's rapidly increasing demand for energy storage (for example, for storing renewable energy or for electric vehicles). Non-aqueous alkali metal–oxygen (AM–O₂: AM=Li, Na and so on) batteries have emerged as promising candidates to replace Li-ion batteries due to their ultrahigh theoretical energy density (several times greater than that of state-of-the-art rechargeable Li-ion batteries) derived from the use of ambient air as the O₂ source and alkali metal (with high theoretical specific capacity and low electrochemical potential) as the anode. However, there are still many challenges in developping a practical AM–O₂ battery^{1–4}.

When a typical aprotic rechargeable AM-O₂ battery discharges, an AM ion is stripped from the AM anode and combines with reduced O₂ at the cathode to form the solid peroxide (Li₂O₂ and NaO₂/Na₂O₂ for Li-O₂ and Na-O₂ batteries, respectively)⁵⁻⁸. This process is reversed on charging. However, during the dischargecharge process, the Li and Na metal, which are 'hostless' anodes, undergo large volume changes, resulting in cracks in the solidelectrolyte interphase (SEI) layer accompanied by large drops in coulombic efficiency and rapid capacity decay9-11. Also, the inhomogeneous distribution of current density on the rough AM anode surface and/or the concentration gradient of Li⁺ or Na⁺ at the SEI inevitably result in Li or Na dendrite formation, which induces battery failure and even fire or explosion events¹²⁻¹⁵. Furthermore, the strong reducibility of Li or Na towards O2 and the electrolyte results in significant parasitic chemistry and electrochemistry reactions during battery cycling, and leads to premature failure.

To achieve stable cycling of the Li or Na electrodeposition/stripping electrochemistry, some very promising approaches have been proposed, including the construction of artificial SEI films¹³, maintaining a sustained supply of Li⁺ in the vicinity of the AM anode surface³, enhancing Li⁺ surface diffusion^{11,14}, using a liquid metal, and so on^{16–18}. Importantly, trace Cs⁺ additive has been used to suppress Li-dendrite growth through an electrostatic shield mechanism^{19,20}. However, most of the above strategies are not very effective in solving both the dendrite growth and oxidation/corrosion problems suffered at the AM anode in Li–O₂ or Na–O₂ batteries.

Theoretically, as Na⁺ has the highest electrochemical redox potential among all AM ions, it can combine with any AM ion except itself to obtain an electrostatic shield. Also, because the electrostatic shield effect of AM ions decreases with increasing ionic radius, Li⁺ is the best candidate. Li-Na alloy can supply Li⁺ on stripping and thus ensure the electrostatic shield effect of Li⁺. Furthermore, compared with other Na-based alloys such as Na-Sb and Na-Sn alloys²¹⁻²³, Li-Na alloy would not sacrifice the specific capacity of the anode because Li and Na metals exhibit similar reaction activities as well as electrolyte compatibility of Li⁺ and Na⁺. Also, alloying Li and Na can improve the corrosion resistance of either Li or Na against O₂ and electrolyte because of the alloy's inherent characteristics^{24,25}. However, developing a Li-Na alloy anode might be difficult because of volume expansion, which causes SEI damage, large internal resistance and low Coulombic efficiency²⁶⁻²⁹.

Here, as a proof-of-concept experiment, we demonstrate a strategy that uses a Li-Na alloy and 1,3-dioxolane (DOL) as anode and additive, respectively, to control dendrite growth and buffer the volume expansion of the alloy anode. By optimizing the Na to Li molar ratio of the alloy, Li-Na alloy anode with a long cycle life is obtained. Although knowing the mechanism is important, the consequences for AM–O₂ batteries are arguably of greater significance. We therefore

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Fig. 1 | Illustration of dendrite and crack suppression. a, In a Li-Na alloy electrode, Li⁺ adsorbs on the tips to repel incoming Na⁺ and forces Na⁺ deposition on adjacent regions away from the tips. At the Na electrode, no Li⁺ is adsorbed on the tips to repel incoming Na⁺ and so Na⁺ deposits on the tips. b, Without DOL, the electrolyte reacts with the alloy to form a rigid SEI that will crack during cycling. After adding DOL, it reacts with the alloy to form an elastic SEI, thus preventing SEI cracking.

made an aprotic bimetallic Li-Na alloy– O_2 battery and achieved a promising electrochemical performance including high capacity and a long cycling stability of 137 cycles, which is four times greater than that of a Na– O_2 battery (31 cycles).

Results and discussion

Design strategy for dendrite- and crack-suppressed Li-Na alloy. The proposed strategy is presented in Fig. 1. Theoretically, on plating, Na⁺ deposits more easily than Li⁺ because of its higher reduction potential (refs ^{30,31}). For our experiment, electrolyte containing only Na⁺ was used for stripping/discharging and depositing/charging of metal (Li, Na or Li-Na alloy) in symmetric or AM–O₂ batteries (Supplementary Figs. 1–4). During discharging in AM–O₂ batteries, for example, most Li⁺ has to be stripped from the anode and migrated to the cathode to combine with the reduced O₂. By contrast, Na⁺ can be obtained by the cathode from the adjacent electrolyte. Therefore, the amount of Li participating in the reaction determines the reaction kinetics of AM–O₂ batteries^{32,33}.

In high-Li-content Li-Na alloys, Li is dominant in the electrochemical reaction, so polarization is severe. During the plating process, the small amount of Na deposition does not favour Na dendrite formation under the strong electrostatic shield effect of Li⁺. Although no dendrites are formed in batteries with Li and high-Li-content-alloy electrodes, the large polarization potential inhibits the practical development of these batteries. When Na is dominant in the Li-Na alloy, the extent of dendrite growth is closely related to the Li content in the alloy. Given that the electrostatic shield effect of Li⁺ is greater than that of Na⁺, because of the small ionic radius of Li⁺, only a small amount of Li in Li-Na alloy will effectively suppress Na dendrites. As the Li content decreases, the small amount of Li⁺ cannot completely prevent Na dendrite growth. Volume variation is an inevitable problem for the hostless Li-Na alloy, leading to SEI cracking accompanied by low Coulomb efficiency and electrolyte depletion. In this regard, DOL could be a promising additive as it can react with the AM electrode to form a robust and highly elastic SEI layer and thus effectively buffer the volume expansion of the AM electrode. However, it cannot eliminate cracking caused by dendrites. So, in AM–O₂ batteries with a Na or an ultralow-Licontent Li-Na alloy electrode, cracks will still appear. Therefore, the Na:Li ratio of the Li-Na alloy is the key factor for dendrite suppression and crack elimination and thus of battery performance.

Characterization of the Li-Na alloy. From its phase diagram, Li-Na alloy is a eutectic alloy, meaning that both components of the alloy retain their individual crystal structures and the alloy does not behave as a solid solution or as intermetallic particles, as shown in Fig. 2a^{34,35}. The structure and morphology of the prepared Li-Na alloys were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD results shown in Fig. 2b demonstrate that the Li and Na in the as-prepared Li-Na alloys with different molar ratios (Na/Li) maintain their individual structures, confirming the immiscibility of the Li-Na alloy. The peak intensity ratio of Na/Li in the XRD patterns increases as the Na/Li value of the alloy increases, further indicating the immiscibility of the Na and Li. The backscattered electron images in Fig. 2c-e, which are closely related to chemical composition and are used to observe the distribution of different elements in an alloy phase, demonstrate that the Li-Na alloy is homogeneous^{36,37}. As the Na/Li value increases, some streaks are observed on the alloy surface. These result from the imperfect sharp edge of the



Fig. 2 | Characterization of the Li-Na alloy. a, Schematics for different alloys. b, XRD patterns of Li, Na and Li-Na alloys with different Na/Li ratios. c-e, Backscattered electron images for Li-Na alloys with Na/Li ratios of 0.6 (c), 6 (d) and 13 (e).

scalpel used to cut the Li-Na alloy ingots and might present potential sites for dendrite growth³⁸.

Despite the immiscibility of the Li-Na alloy, it still exhibits an alloy nature, such as its resistance to oxygen and the electrolyte. When Na metal and Li-Na alloy (Na/Li = 6) were exposed to organic solvent and trace O_2 for 5 days in a glove box, the Na metal surface underwent severe oxidation, whereas the Li-Na alloy still exhibited a metallic lustre without any change. This observation is consistent with observations of Na metal and Li-Na alloy soaked in 0.5 M NaCF₃SO₃/tetraethylene glycol dimethyl ether (TEGDME) electrolyte, demonstrating the oxidation and corrosion resistance of the alloy (Fig. 3a).

Electrochemical impedance spectroscopy (EIS) results for Li-Na alloys and individual Li and Na metals soaked in electrolyte for 3 h are shown in Fig. 3b. Na has the largest impedance among the investigated metals due to the formation of a passivation film with high impedance. For the Li-Na alloy, the impedance decreases with decreasing Na/Li ratio. When the Na/Li value is 6, the impedance of the alloy is less than that of Li, demonstrating the Li-Na alloy's strong corrosion resistance towards the electrolyte, even though the alloy contains only a small amount of Li.

To evaluate the effect of our strategy on Na dendrite suppression and crack elimination, the deposition behaviors of Li, Na and their alloys were examined in symmetrical batteries using $0.5 \text{ M} \text{ NaCF}_3\text{SO}_3/\text{TEGDME}$ or $0.5 \text{ M} \text{ NaCF}_3\text{SO}_3/\text{DOL}/\text{TEGDME}$ (DOL:TEGDME = 1:1 by volume) as the electrolyte (Fig. 3c). After five cycles of stripping/plating at a current density of 1 mA cm⁻² under a capacity of 2 mAh cm⁻², an inspection of the metal electrodes was conducted by SEM, as shown in Fig. 3d-i and Supplementary Fig. 5. In the batteries with 0.5 M NaCF_3SO_3/TEGDME electrolyte, the electrodes with Li or a high-Li-content alloy are typically flat but cracked. The alloy electrode surface with a Na/Li value of 6 (that is, low Li content) is still flat, but cracked after cycling (Fig. 3f), demonstrating that the Li-Na alloy electrode with a small amount of Li can effectively suppress dendrite growth. When the value of Na/Li

is 13, a rough surface with dendrites and large cracks is observed, similar to the surface of the Na anode, indicating that ultralow Li or a lack of Li cannot prevent dendrite growth (Fig. 3h). By contrast, in the batteries using 0.5 M NaCF₃SO₃/DOL/TEGDME electrolyte, Li and Li-Na alloys with Na/Li values of 0.6 and 6 present flat surfaces with no cracks after stripping/plating cycling (Fig. 3e–g), whereas Na and Li-Na alloy electrodes with an Na/Li value of 13 are still rough and cracked (Fig. 3i), demonstrating that the SEI formed in 0.5 M NaCF₃SO₃/DOL/TEGDME electrolyte can buffer volume change but not eliminate cracks caused by dendrite growth.

We also verified the role of charge carriers in battery operation. When the alloy battery was run in pure TEGDME and DOL/TEGDME solvents, no capacity was observed, and the battery quickly failed, demonstrating the importance of the charge carriers (Supplementary Fig. 6).

Cyclic response of Li-Na alloy in symmetric batteries. To evaluate the electrochemical performance with the above strategy, we subjected the assembled symmetric batteries to a cyclic stripping/plating process under constant current density (0.5 mA cm^{-2}). Each cycle was set to 2h. As shown in Fig. 4a, in $0.5 \text{ M} \text{ NaCF}_3\text{SO}_3/\text{TEGDME}$ electrolyte, the battery with a Li-Na alloy (Na/Li=6) electrode ran for more than 130 h with rapidly increasing voltage hysteresis, indicating instability of the SEI layer, and thus leading to a large polarization. In sharp contrast, the other batteries ran for much less than 130 h and suffered from much larger voltage hysteresis. Specifically, an abrupt voltage drop occurred after a dramatic voltage increase in the Na and low-Li-content-alloy (Na/Li=13) batteries, which was ascribed to a short circuit of the batteries induced by the formation of Na dendrites. These results demonstrate that alloying can improve Na electrode stability to some degree.

When the symmetric batteries were tested in the 0.5 M NaCF₃SO₃/DOL/TEGDME electrolyte (Fig. 4b), the Li-Na alloy (Na/Li=6) symmetric battery ran for more than 800h without obvious voltage hysteresis. The other batteries, including Li and

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Fig. 3 | Oxidation and corrosion resistance as well as metal electrode morphology. a, Optical photographs of the Li-Na alloy and Na after undergoing different treatments. **b**, EIS results for Li/Cu, Li-Na alloy/Cu and Na/Cu batteries after resting in electrolyte for 3 h. Inset, enlarged EIS of a Li-Na alloy/Cu battery. **c**, Schematic for a symmetric battery. **d-i**, SEM images for Li (**d**,**e**), Li-Na alloy with a Na/Li molar ratio of 6 (**f**,**g**) and Na (**h**,**i**) electrodes after five stripping/plating cycles in 0.5 M NaCF₃SO₃/TEGDME or NaCF₃SO₃/DOL/TEGDME electrolyte.

high-Li-content-alloy (Na/Li=0.6) batteries, exhibited a large polarization potential; this performance, as well as the high cost of Li, hampers the application prospects of these batteries despite their improved cycle life. By contrast, Na and low-Li-content-alloy (Na/ Li=13) batteries exhibited slightly improved cycle life but gradually increasing overpotential on cycling; this overpotential cannot be resolved because of the cracks caused by Na dendrites growth. In general, after the introduction of DOL into the electrolyte, both the stability and cycle life of the batteries were enhanced. We attribute this enhancement to the elastic SEI layer formation by DOL reacting with these electrodes. By tracking electrode morphology evolution during the cycling process, it was found that the Na electrode shows gradually growing dendrites, while the alloy (Na/Li=6) electrode presents almost no dendrites and cracks (Supplementary Fig. 7). To further elucidate the dendrite suppression effect, we monitored alloy (Na/Li=6) and Na electrode plating/stripping in a home-made transparent battery using an optical microscope^{3,12}. Before cycling, the two electrodes appear to have a smooth surface. On cycling, protrusions start to appear on the Na electrode, indicating dendrite formation (Supplementary Fig. 8). These protrusions nucleate and grow into much large dendrites that are very distinct at the 40th cycle. In contrast, the alloy electrode exhibits no dendrites. To further proving the superiority of Li metal addition into Na for dendrite suppression, we tested the stability of the Na electrode in 0.5 M NaCF₃SO₃/DOL/TEGDME electrolyte containing 0.05 M Li⁺. The voltage profiles for a Na|Na symmetric battery containing 0.05 M

Li⁺ electrolyte show a few cycles before battery failure, which is due to dendrite formation, as verified by in situ optical microscope observations (Supplementary Figs. 9 and 10).

To verify the elastic SEI layer formation, we analysed the SEI composition by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). As shown in Supplementary Fig. 11, the FTIR spectrum of the SEI in 0.5 M NaCF₃SO₃/DOL/TEGDME electrolyte shows two additional peaks at 1,082 and 1,144 cm⁻¹, corresponding to DOL and poly(1,3-dioxolane), respectively, indicating elastic SEI formation^{38,39}. The Na1s, S2p, F1s, Li1s, C1s and O1s XPS spectra for SEI on the cycled alloy (Na/Li=6) surface are presented in Supplementary Fig. 12. Na1s, S2p, F1s and Li1s XPS spectra for the SEI formed in 0.5 M NaCF₃SO₃/DOL/TEGDME electrolyte are consistent with those in 0.5 M NaCF₃SO₃/TEGDME electrolyte. However, the C1s and O1s XPS spectra are not consistent. Specifically, a stronger C-O binding energy is observed in the C1s (286 eV) and O1s (532 eV) spectra in NaCF₃SO₃/DOL/TEGDME electrolyte than in the NaCF₃SO₃/ TEGDME electrolyte, indicating poly(1,3-dioxolane) formation^{40,41}. EIS also shows that in DOL-containing electrolyte, the interfacial resistance undergoes a slight increase during the cycle process (quite contrary to that for the electrolyte containing no DOL (Fig. 4c,d)) manifesting no dendrites and compact SEI formation⁴².

Electrochemical performance of metal-O₂ batteries. Electrochemical tests of metal-O₂ batteries using Li-Na alloy (Na/Li=6) as well as Li or



Fig. 4 | Electrochemical performance for symmetric batteries. a,b, Voltage profiles for symmetric batteries in 0.5 M NaCF₃SO₃/TEGDME (**a**) and NaCF₃SO₃/DOL/TEGDME (**b**) electrolytes. **c,d**, Electrochemical impedance spectra of symmetric batteries using Li-Na alloy (Na/Li=6) after the 1st, 30th and 60th cycles in 0.5 M NaCF₃SO₃/TEGDME electrolyte (**c**) and after the 1st, 200th and 400th cycles in 0.5 M NaCF₃SO₃/DOL/TEGDME electrolyte (**d**).

Na as the anode were conducted in $0.5 \text{ M} \text{ NaCF}_3\text{SO}_3/\text{DOL}/\text{TEGDME}$ electrolyte using commercial carbon nanotubes (CNTs) as the cathode. Figure 5a presents cyclic voltammetry (CV) profiles of these metal–O₂ batteries. The onset potential (2.42 V) for the oxygen reduction reaction in the Li-Na alloy–O₂ battery is between those for the Li–O₂ (2.66 V) and Na–O₂ (2.27 V) batteries, indicating the occurrence of Li–O₃ and Na–O₃ battery reactions.

The free discharge-charge curves of the metal-O₂ batteries are presented in Fig. 5b. First, the discharge potential of the Li-O₂ battery reaches 2.55 V, which is much lower than that of the battery with Li⁺ electrolyte because of kinetic polarization. The initial discharge potential of the alloy-O₂ battery is higher than that of the Na-O₂ battery because the discharge potential of the alloy-O2 battery lies between those of the Li-O₂ and Na-O₂ batteries. Second, the charge curve of the alloy-O₂ battery is more like that of the Na-O₂ battery because Na is the main component. Supplementary Table 2 presents the calculated equilibrium potential of the metal-O₂ battery, which is slightly higher than the initial discharge potential in Fig. 5b. When these batteries were subjected to a galvanostatic test with a capacity of 1,000 mAhg⁻¹, the effect of the alloy anode was conspicuous (Fig. 5c): the alloy-O₂ battery managed 137 cycles before its discharge potential decreased to 1.6 V, representing the longest cycle life ever reported in a Na–O₂ battery with CNTs as the cathode (Supplementary Table 4)43. By contrast, the Li-O2, Na-O2 and other alloy (Na/Li=0.6 or 13) batteries only achieved 34, 31, 45 and 32 cycles, respectively (Supplementary Fig. 13).

The evolution of the morphology of the Li-Na alloy and Na anodes in metal– O_2 batteries was recorded, as shown in Supplementary Figs. 14 and 15. The Li-Na alloy surface was smooth and compact even after 130 cycles, whereas the Na anode became rough and cracked as cycling proceeded, demonstrating the stability of Li-Na alloy anode. XRD patterns for the cycled alloy anodes revealed a rapid increase in the NaOH peak intensity with increasing cycle number in 0.5 M NaCF₃SO₃/TEGDME electrolyte. By contrast, the patterns of alloy anodes cycled in 0.5 M NaCF₃SO₃/DOL/TEGDME electrolyte showed a slow increase (Supplementary Fig. 16), indirectly demonstrating that the formed compact SEI prevents the inner Na from corroding⁴⁴.

We then used SEM and XRD to analyse the reversibility of the discharge products in the three metal-O₂ batteries. The SEM images demonstrate that, in the Li-O₂ battery, the morphology of the discharge products is toroid-like. Indeed, similar observations have been reported previously for a Li-O2 battery using Li⁺ electrolyte (Fig. 5d,e)⁴⁵. In the alloy- O_2 battery, both toroid-like and small-particle discharge products appear. By contrast, in Na-O₂ battery, only small-particle discharge products are observed, further demonstrating the occurrence of Li-O₂ and Na-O₂ battery reactions in the alloy-O2 battery (Fig. 5f,g). Li and Na ions are well known to produce red and yellow flames³⁰, respectively, so we used a qualitative flame test to detect the presence of Li and Na discharge products on the CNTs cathodes, as shown in the insets of Fig. 5d-g. In the Li-O₂ battery, the discharge products resulted in a red flame, but in the Na-O₂ battery they produced a yellow flame. In the alloy-O₂ battery, the flame was a mixed red and yellow flame. Thus, both SEM and flame analysis demonstrated the occurrence of Na-O2 and Li-O2 battery reactions in alloy-O2 batteries. The XRD results in Fig. 5h also demonstrated the existence of both Li₂O₂ (JCPDS 09-0355) and Na₂O₂·2H₂O (JCPDS 15-0064) in the alloy-O₂ batteries after discharge, consistent with the aforementioned SEM and flame tests. These products decomposed completely after charging (Supplementary Figs. 17 and 18), demonstrating their reversibility46

Variation of the content of Li⁺ and Na⁺ on the CNTs cathodes was recorded during the discharge–charge processes using inductively coupled plasma (ICP) spectrometry. As shown in Fig. 5i, the Li⁺ and Na⁺ contents simultaneously increased during the discharge process and subsequently gradually decreased during the charge process, indicating that both Li and Na underwent redox reactions during the electrochemical process. SEM images for discharge product evolution in an alloy–O₂ battery show the redox reactions of Li and Na towards O₂ (Supplementary Fig. 19), consistent with

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Fig. 5 | **Electrochemical characterization for metal-O**₂ **batteries. a**, CV curves for metal-O₂ batteries at a scan rate of 0.1 mV s^{-1} between 1.9 and 4.2 V. **b**,**c**, Galvanostatic tests for metal-O₂ batteries at a current density of 200 mA g⁻¹: free discharge-charge curves (**b**) and cycling performance (**c**) at a capacity limitation of 1,000 mA hg⁻¹. **d-g**, SEM images (insets show corresponding flame responses) of the CNTs cathode: pristine (**d**) and discharged cathodes using Li (**e**), Li-Na alloy (Na/Li=6) (**f**) and Na (**g**) as anode. **h**, Corresponding XRD patterns for discharge products on CNTs cathodes in batteries using different anodes. **i**, Variation of Li and Na content on the CNTs cathode during the discharge-charge process in alloy-O₂ batteries. Inset, corresponding discharge-charge curve.

the aforementioned ICP results. Thus, the stripping and plating of Li and Na is key to suppressing dendrite formation.

Despite the enhanced cycling performance of the alloy– O_2 battery, it still shows fading after 137 cycles. To determine the reasons for this fading, SEM, ¹H NMR and XPS were used to analyse the faded battery. An SEM image of the cycled CNTs cathodes demonstrated severe coating with side products (Supplementary Fig. 20), and ¹H NMR spectra of the cycled separator revealed some side products (Supplementary Fig. 21). The XPS data showed an increased O signal in the C1s spectra of the CNTs cathode after cycling (Supplementary Fig. 22). All these results suggest that an unstable CNTs cathode and electrolyte may be the reason for the fading. To further verify this, the alloy anode from the faded battery was reassembled with a fresh CNTs cathode and electrolyte to form a new battery. The new battery ran for another 93 cycles with voltage profiles that were almost identical to those of the original battery (Supplementary Fig. 23), confirming the above supposition.

To improve the overall performance of the above metal– O_2 batteries, a RuO₂/CNT catalyst was designed and synthesized to promote the O₂ reduction/evolution reaction during the discharging/ charging processes (Supplementary Figs. 24 and 25). Interestingly, with RuO₂/CNT, the Li-Na alloy–O₂ battery achieved a cycle life of more than 250 cycles, accompanied by a charge potential lower

than 3.4 V (Supplementary Fig. 26). Furthermore, by introducing RuO_2/CNT or Co/NCF catalysts, the rate performance of the alloy- O_2 battery can also be improved (Supplementary Fig. 27).

Conclusion

Our study demonstrates the critical role of the Li-Na alloy anode and electrolyte additive (DOL) in stabilizing the Li or Na plating/stripping electrochemistry. By optimizing the Na/Li value of the alloy, we have obtained a dendrite-suppressed, oxidation-resistant and crack-free Li-Na alloy anode, as verified by analysis of its morphology evolution and SEI composition, thus realizing an alloy anode with a long cycle life. When an alloy with optimal ratio was used, a proposed aprotic bimetallic Li-Na alloy– O_2 battery with good cycling stability was realized. By analysing the evolution of discharge products in the Li-Na alloy– O_2 battery, we found that the stripping and plating of Li and Na are key for suppressing dendrites. This study also provides guidance for developing bimetal batteries such as bimetal ion batteries, and bimetal–S/Se batteries, which may possess new chemistries and exhibit much better electrochemical performance than monometal batteries.

Data availability

The authors declare that all the data supporting the findings of this study are available within the paper and its Supplementary Information.

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Author contributions

X.B.Z., J.M.Y., Y.Z. and J.L.M. developed the research concept. J.M.Y. designed the Li-Na alloy and catalyst, and J.L.M. then prepared the materials. X.B.Z. designed the electrochemical experiments, which J.L.M and Y.Y. performed. X.B.Z., J.M.Y., Y.Z., J.L.M. and F.L.M. contributed to interpretation of the results and wrote the manuscript, and all authors contributed to the scientific discussion.

Competing interests

The authors declare no competing interests.

Additional information

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