

Research Highlight

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# Recharging calcium-oxygen batteries

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Calcium-oxygen (Ca-O<sub>2</sub>) batteries have attracted increasing attention due to their high abundance and theoretical specific capacity. However, the reversible Ca-O<sub>2</sub> battery under room temperature remains unsuccessful due to the inert nature of discharge products (CaO) and the corresponding sluggish four-electron reaction kinetics. This preview highlights a flexible and rechargeable Ca-O<sub>2</sub> battery at room temperature, enabled by optimized ionic liquid electrolytes that achieve efficient two-electron redox reactions, leading to the formation of a chemically reactive discharge product (CaO<sub>2</sub>). Moreover, we further speculate and analyze this transformation of the oxygen reduction reaction (ORR) mechanism.

With the increasing demand for energy density, new high-specific energy batteries continue to emerge<sup>[1]</sup>. Among various energy storage devices, reversible metal-oxygen batteries have attracted increasing attention due to their low cost, environmental friendliness, and higher volumetric energy densities than state-of-the-art lithium-ion batteries<sup>[2,3]</sup>. The Li-O<sub>2</sub> and Na-O<sub>2</sub> battery systems have garnered significant attention and made great progress due to the active research on lithium-metal- and sodium-metal-based batteries. In contrast, other multivalent metal-O<sub>2</sub> systems, such as Mg-O<sub>2</sub> and Ca-O<sub>2</sub>, which offer higher theoretical



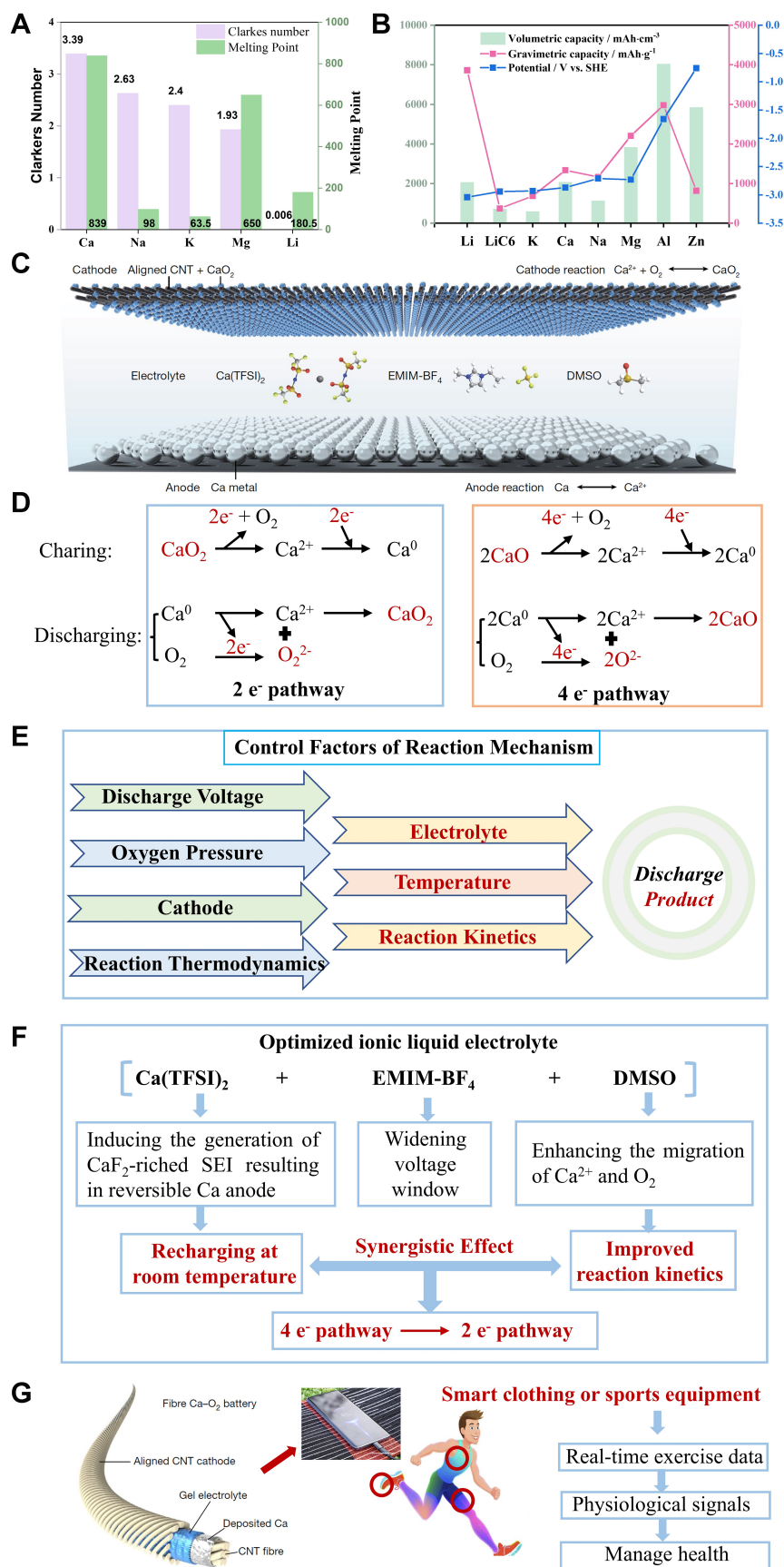
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energy densities, have received limited attention. However, it is worth noting that Ca is the fifth most abundant element in the Earth's crust (3.39%, more than 150% of the abundance of Na and Mg) and possesses a high melting point (839 °C), making it a promising candidate for applications across a wide temperature range, as shown in Figure 1A. Additionally, its low molecular weight (40.078 g·mol<sup>-1</sup>) and the low reduction potential of Ca<sup>2+</sup>/Ca at -2.87 V [vs. standard hydrogen electrode potential (SHE)] further highlight Ca as a highly competitive metal in metal-O<sub>2</sub> batteries. Furthermore, Ca has a high theoretical volumetric capacity (2,073 mAh·cm<sup>-3</sup>), meaning that it can match lithium metal batteries in terms of performance [Figure 1B]. However, the development of Ca-O<sub>2</sub> batteries seems to stagnate due to irreversible Ca plating/stripping and inert discharge products (CaO) resulting from sluggish four-electron reactions<sup>[4,5]</sup>. These challenges make the cells nearly non-rechargeable (< 10 cycles) and cause extremely large cell polarization at both elevated and room temperatures<sup>[6]</sup>.

As is well known, the electrolyte plays a crucial role in maintaining electrode stability and accelerating the reaction kinetics, which can change the ORR mechanism. For a multivalent Ca metal anode in organic electrolytes, the solvent tends to be consumed, generating passivating layers that inhibit plating and stripping. For example, in propylene carbonate, butyrolactone and acetonitrile-based electrolytes, the typical passivating byproducts of Ca(OH)<sub>2</sub>, CaCO<sub>3</sub> and calcium alkoxides are easily generated. Under elevated operating temperatures (75-100 °C) in organic electrolytes, the reversible deposition of Ca metal could be achieved to a certain extent<sup>[7]</sup>. A recent research in *Nature* by Prof. Peng introduced a novel ionic liquid electrolyte in Ca-O<sub>2</sub> batteries, which could be reversibly operated over 700 cycles at room temperature<sup>[8-10]</sup>. The Ca-O<sub>2</sub> battery consists of a Ca metal anode, an aligned carbon nanotube (CNT) sheet air cathode, and a dimethyl sulfoxide (DMSO)-based ionic liquid electrolyte, as shown in Figure 1C. This electrolyte is 0.5 M calcium bis(trifluoromethanesulfonimide) [Ca(TFSI)<sub>2</sub>] dissolved in a 1:1 volume mixture of ionic liquid 1-ethyl-3-methylimidazole tetrafluoroborate (EMIM-BF<sub>4</sub>) and DMSO. This optimized electrolyte enables a highly reversible two-electron ORR mechanism for the priority formation of CaO<sub>2</sub> instead of a sluggish four-electron reaction during the discharge process at room temperature. The details of two- and four-electron pathways are shown in Figure 1D. To verify this O<sub>2</sub> reduction mechanism, the corresponding powder X-ray diffraction (XRD) spectra of the cathodes after discharge and charge processes exhibit the reversible loss and regeneration of the CaO<sub>2</sub> signal. The results of differential charge density calculations indicate that CaO<sub>2</sub> exhibits better electron transfer than CaO, facilitating the reduction of O<sub>2</sub>. As for the O<sub>2</sub> reduction pathways at room temperature, density functional theory calculations show that the two-electron mechanism has a lower Gibbs free-energy difference ( $\Delta G_{\text{CaO}_2} = -1.43$  eV) compared to the four-electron mechanism ( $\Delta G_{\text{CaO}} = -0.53$  eV), which can be attributed to the absence of O-O bond cleavage during the formation of CaO<sub>2</sub>. Therefore, the thermodynamics and kinetics of this two-electron mechanism are conducive to the cycle reversibility of batteries.

According to the cryogenic transmission electron microscopy (CRYO-TEM) images and X-ray photoelectron spectroscopy (XPS) depth profiling of the anode disassembled from a recharged battery, commercially available Ca(TFSI)<sub>2</sub> could aid in the generation of CaF<sub>2</sub>-rich solid-electrolyte interphase (SEI) for reversible Ca anodes. This SEI comprises small crystalline CaF<sub>2</sub> domains within surrounding amorphous organic compounds, including -SO<sub>x</sub>R (derived from DMSO and TFSI), -CF<sub>x</sub> (derived from TFSI) and a small proportion of -CO<sub>2</sub>, which contribute to the Ca<sup>2+</sup> conductivity and form the foundation for the operation of Ca-O<sub>2</sub> batteries at room temperature. Meanwhile, the ionic liquid EMIM-BF<sub>4</sub> and DMSO are used to widen the voltage window and improve the migration of Ca<sup>2+</sup> and O<sub>2</sub> to enhance kinetics. The Raman spectroscopy revealed that the interaction between Ca<sup>2+</sup>-BF<sub>4</sub><sup>-</sup> and Ca<sup>2+</sup>-TFSI<sup>-</sup> in the EMIM-BF<sub>4</sub>/DMSO (50:50 vol%) electrolyte is the weakest. It means the reduced contact ion pairs in Ca<sup>2+</sup> coordination, which results in a decreased Ca<sup>2+</sup> de-solvation energy barrier of 30.37 KJ·mol<sup>-1</sup> for enhanced reversibility of Ca metal anodes.



**Figure 1.** (A) Clarkes number and melting point of representative alkaline-earth and alkali metals; (B) Gravimetric and volumetric capacities of alkaline-earth and alkali metals with the redox potentials; (C) Schematic diagram of ionic liquid electrolyte-based Ca-O<sub>2</sub> battery; (D) The details of two-electron and four-electron pathways; (E) The control factors of the reaction mechanism for Li-O<sub>2</sub> battery; (F) The possible logic diagram for the change from a four-electron to two-electron pathway; (G) The applications of flexible Ca-O<sub>2</sub> batteries on wearable fields.

The above characterization results verify the transition from four- to two-electron ORR. However, it seems that the factors controlling the above-mentioned reaction mechanisms are not directly addressed in the paper. Considering the similarity in the ORR mechanism for Li-O<sub>2</sub> and Ca-O<sub>2</sub> batteries, we can speculate on the determining factors behind the change of discharge products. The factors controlling reaction mechanisms for Li-O<sub>2</sub> batteries include the discharge voltage, oxygen pressure, cathode, reaction thermodynamics, electrolyte, temperature and reaction kinetics, which have important effects on discharge products<sup>[11-14]</sup>, as shown in Figure 1E. For example, the introduction of catalysts in the cathode of light-assisted Li-O<sub>2</sub> batteries drives exciton dissociation and activates O<sub>2</sub> for superoxide ( $\bullet\text{O}_2^-$ ) radicals, rather than singlet oxygen ( $^1\text{O}_2$ ) under photoexcitation, which regulate the discharge product<sup>[15]</sup>. It is well known that the operating temperature of previously reported Ca-O<sub>2</sub> batteries needs to be high to improve the reversibility of the decomposition of the discharge product, CaO. However, the Ca(TFSI)<sub>2</sub> component of this optimized ionic-liquid electrolyte effectively promotes the generation of CaF<sub>2</sub>-rich SEI for reversible Ca anodes, making the Ca-O<sub>2</sub> battery feasible to operate at room temperature. Conventional Ca-O<sub>2</sub> cells with conventional organic electrolytes also require high operating temperatures to increase the reversibility of Ca metal anodes. As is well known, the operating temperature is an important factor influencing the reaction mechanism. Additionally, the DMSO of the optimized ionic-liquid electrolyte improves the migration of Ca<sup>2+</sup> and O<sub>2</sub>, which effectively enhances reaction kinetics. Thus, due to the synergistic effect of reduced operating temperature and improved reaction kinetics, the reaction mechanism successfully transforms from a four-electron to a two-electron pathway, as shown in Figure 1F.

Thanks to this durable ionic-liquid electrolyte, the Ca-O<sub>2</sub> batteries exhibit similar and stable behaviors in air or pure O<sub>2</sub> at room temperature, with a cycle life of 450 times in air (at 1 A·g<sup>-1</sup> and 500 mAh·g<sup>-1</sup>). Given the satisfied cycle stability, low tendency of Ca metal to form dendrites, and air-resistant ionic liquid electrolyte, which meet the requirements of wearable electronic devices with safety and sustainability, the authors assembled a flexible Ca-O<sub>2</sub> fiber battery by coating a calcium-deposited CNT fiber anode with an ionic liquid gel electrolyte and then wrapping a neatly arranged CNT cathode sheet on the outside of the fiber. The deposition of Ca onto the flexible CNT fiber avoids the use of excessive Ca metal, and the poor workability of the overall Ca metal used in traditional flat Ca batteries. When bent from 0° to 180°, the fiber battery continues to discharge steadily and remains stable at about 1.7 V. The authors used a commercial knitting machine to weave these fiber cells into breathable, flexible battery textiles that can power electronic devices such as mobile phones. Its success raises hopes for the application of Ca-O<sub>2</sub> batteries in wearable and biocompatible devices, as shown in Figure 1G. This flexible battery can be easily integrated into sports equipment, such as sports shoes, sports clothes, bracelets, smart helmets, *etc.*, or can be directly attached to the skin, through which the wearer can monitor real-time exercise data for physiological signals such as heart rate, blood pressure, body temperature. In addition, flexible Ca-O<sub>2</sub> batteries make smart clothing possible, which can monitor body posture, movement range, breathing and other data.

In conclusion, the authors report for the first time a flexible and reversible Ca-O<sub>2</sub> battery operating at room temperature. Through comprehensive characterization, they attribute the excellent performance of rechargeable Ca-O<sub>2</sub> batteries to the new and efficient two-electron ORR mechanism which favors the



formation of CaO<sub>2</sub>. Meanwhile, the optimized ionic liquid electrolyte effectively promotes the generation of CaF<sub>2</sub>-rich SEI for a reversible Ca anode, widens the voltage window and improves the migration of Ca<sup>2+</sup> and O<sub>2</sub>, thereby enhancing reaction kinetics. Due to the synergistic effect of reduced operating temperature and improved reaction kinetics, the discharge product successfully changes from CaO to CaO<sub>2</sub>. In addition, the flexible Ca-O<sub>2</sub> battery textiles successfully power the mobile phone, verifying the feasibility in next-generation wearable systems. Further, the following research fields are worth exploring in depth to improve the electrochemical performance of Ca-O<sub>2</sub> batteries. For example, the ionic liquid electrolyte is further optimized to possess high ionic conductivity for the reversible plating/stripping cycles at high current densities. The structure of CNT-based cathodes also warrants further design to facilitate the migration of O<sub>2</sub> and discharge products for avoiding clogging and battery failure. The Ca metal anode plays a vital role in the cycle reversibility and lifetime of Ca-O<sub>2</sub> batteries and is well worth further optimization and improvement. Regarding two- and four-electron reaction mechanisms of Ca-O<sub>2</sub> batteries, what are the key controlling factors? Under what conditions will two-electron reactions dominate, and under what conditions will four-electron reactions prevail? Additionally, do the materials and manufacturing methods used in the Ca-O<sub>2</sub> battery textiles offer cost and energy efficiency advantages, making them favorable for large-scale implementation of Ca-O<sub>2</sub> battery technology? What are the current challenges facing this technology? These problems and challenges are worth further exploration.

## DECLARATIONS

### Authors' contributions

Drafted the manuscript: He, X.

Revised and rewrote sections of the manuscript: He, H.; Zhang, K.; Li, F.

### Availability of data and materials

Not applicable.

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### Conflicts of interest

All authors declared that there are no conflicts of interest.

### Ethical approval and consent to participate

Not applicable.

### Consent for publication

Not applicable.

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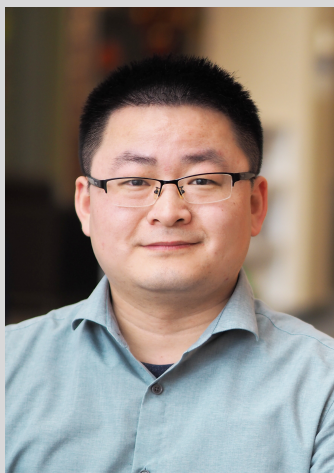
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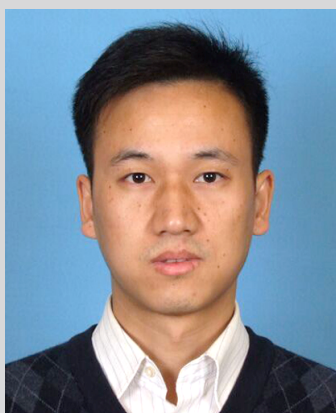
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