



Views & Comments

Key Technology and Engineering Development of Multi-Electron Battery Systems

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1. Introduction: Opportunities for new energy systems

With the rapid development of next-generation technologies—including the Internet, information technology, quantum technology, micro–nano technology, big data, and artificial intelligence—human civilization is rapidly moving toward an intelligent era (following the electrification and information age). The evolution of clean energy structures, electrical transportation, and intelligent power grids, which are establishing new low-carbon, safe, and efficient energy systems, is driving the development of the intelligent era and the key technologies with which to realize emission peak and carbon neutrality goals.

Guided by the demands of a national energy strategy, multi-electron battery systems are focused on next-generation energy-dense storage technology, which boast both long life and improved safety [1]. Research on novel electrochemical energy storage and multi-electron reaction mechanisms, building multi-ion synergies, and broadening the scope of multi-electron material research [2,3], can greatly increase battery energy densities, which can consequently help the renewable energy industry build new high-performance battery systems. The key technologies and implementation strategies for a novel multi-electron battery system are described in this study.

2. Theory: Novel technology and current multi-electron battery system challenges

In 2002, the National Basic Research Program of China funded the “fundamental research on new green secondary batteries” National Basic Research Program of China (973 Program), which first proposed the concept of “multi-electron reaction.” Compared to aqueous Zn/MnO₂ and lead-acid batteries, ferrate-based electrode materials provide three-electron transfer in an electrochemical process to obtain higher energy density, which suggests the potential application of multi-electron materials in the battery field.

The energy density of an electrode material (E_D) can be calculated using the extended Nernst equation, as follows:

$$E_D = \frac{\Delta_r G^\theta}{\sum M_i} = - \frac{nF\varepsilon}{\sum M_i} \quad (1)$$

where n denotes the number of charge transfers per mole reaction; F denotes the Faraday constant; ε denotes the thermodynamic equilibrium voltage or electromotive force (emf) in general; $\sum M_i$ denotes the sum of the mole weights or volumes of the reactants; and $\Delta_r G^\theta$ denotes the Gibbs formation energy of the reactant.

It can be confirmed that the high specific energy of electrode materials is directly related to the number of electrons involved in the reaction. The periodic table of multi-electron elements with multi-electron reaction characteristics was systematically compiled in 2016, thereby clarifying the multi-electron reaction rules under various reaction modes [2]. Moreover, the thermodynamic characteristics and kinetic optimization technologies in the multi-electron reaction process were discussed in 2020 [3]. The realization of multi-electron reversible reaction characteristics of high specific energy electrode materials for different energy storage systems and electrochemical reaction modes is a key technology for innovation and development in the field.

Through continuous exploration in recent years, new multi-electron battery systems based on light elements and multi-electron reaction mechanisms have attracted considerable attention owing to their higher energy density (via Na⁺, K⁺, Mg²⁺, and Al³⁺ charge carriers) and chemical reactions involving anions (O²⁻ and S²⁻) [4,5]. Lithium–air (Li–O₂) and lithium–sulfur (Li–S) batteries are expected to achieve extremely high energy density, approximately 2–10 times more than those of current lithium-ion batteries [6]. Energy density thermodynamic calculations of viable battery systems and advanced energy storage materials reveal that the theoretical energy density of these multi-electron battery systems is greater than that of traditional single-electron battery systems. In particular, full cells assembled from metallic lithium and conversion-/alloy-type electrodes with highly electronegative elements and light weight have great potential for realizing highly specific energy storage systems [3].

This is one of the most important technical trends in multi-electron battery system applications.

Nevertheless, the actual energy density of multi-electron electrodes is much lower than the theoretical energy density because of the poor dynamic properties and stability of electrode materials. The low electrical conductivity and poor wettability of the electrode/electrolyte interface limits its dynamic performance. Moreover, the volume expansion and grain pulverization directly restrict its electrochemical reaction kinetics. Multi-electron battery systems face substantial challenges in terms of constructing electrode/electrolyte interface chemical compatibility, high-loading active-material composite-electrode stability, and high-specific-energy metal-anode reliability from the perspectives of battery integration and practical engineering application. The electrode/electrolyte interface can be prone to generating higher interfacial impedances, metal dendrites, and battery degradation owing to the multiscale physical and electrochemical interactions between the electrolyte and electrode.

High-loading active-material composite electrodes are the basis for realizing higher-specific-energy batteries. However, they can cause severe electrode polarization and substantial degradation of the reversible specific capacity. The irreversible parasitic reactions between the highly reactive metal anodes and electrolytes can be major constraints limiting the high specific energy and long cycle performance of multi-electron battery systems. Moreover, the engineering development of multi-electron battery systems faces challenges in terms of manufacturing costs and large-scale production.

3. Methods: Feasible solutions to multi-electron battery system applications

3.1. Electrode/electrolyte interface chemical compatibility construction

The multi-electron battery system is driven primarily by electrochemical reactions at the electrode/electrolyte interface along with the migration of charge carriers. Electrode wettability, interface stability, and charge carrier migration at the electrode/electrolyte interface play important roles in improving the cycle performance and prolonging the life of the battery. Physicochemical interactions at the electrode/electrolyte interface directly affect the electrochemical performance, whereas poor mechanical stability during cycling aggravates parasitic interface reactions. Moreover, slow ion migration can lead to a large interfacial impedance and degradation of the battery capacity. Additionally, an uneven deposition of charge carriers on the metal anodes can result in short circuits within the battery.

In view of the aforementioned problems, artificial interface layers with high mechanical strength constructed via magnetron sputtering [7], atomic layer deposition [8], and electrolyte additive modification [9] can effectively inhibit the surface side reactions and induce the uniform deposition of carriers at laboratory scale. However, economical electrode modification processes in large-scale production, such as chemical vapor deposition, still need to be developed. From multi-electron cathode material perspective, reducing the internal stress of materials and constructing a fast ion transport channel using heterogeneous component interfacial layer design can substantially improve cycling stability [10]. Additionally, the optimal electrolyte usage and negative/positive electrode capacity (N/P) ratio are crucial for alleviating side reactions on multi-electron electrodes, thus reducing ion consumption in the electrolyte and improving the energy output of multi-electron battery systems.

3.2. High-loading active material electrode design

A thick-electrode design can efficiently provide high-loading active material electrodes, which is vital for obtaining a high

energy density. In a previous study, when the electrode thickness was increased from 25 μm (active material loading of 8 $\text{mg}\cdot\text{cm}^{-2}$) to 200 μm (64 $\text{mg}\cdot\text{cm}^{-2}$), the inactive component ratio decreased from 44% to 12%, thus resulting in a substantial increase in the proportion of active material and an improvement in the energy density of the battery [11]. However, the ion transport distance increases with increasing electrode thickness, which results in poor electrochemical reaction kinetics and reduced performance. Additionally, owing to the limitations of typical slurry coating techniques, an increase in internal stress during the drying process unexpectedly affects the electrode structure, thereby posing considerable challenges to the practical application of thick electrodes.

Fortunately, low-tortuosity thick electrodes constructed using external magnetic field regulation, directional freeze drying, and three-dimensional (3D) printing technology can improve the wettability of the electrolyte and the ion transfer rate at laboratory scale, thereby providing valuable research insight into the engineering application of thick electrodes. Additionally, the mechanical stability and charge transfer performance of the electrode can be considerably enhanced using a 3D integrated electrode structure design. Consequently, large-scale production and economical thick-electrode manufacturing processes are likely to gain considerable attention in future.

3.3. High-stability metal anode preparation

Multi-electron metal anodes with high theoretical specific capacities are considered to be an ideal choice for next-generation battery systems, but they present great challenges in terms of safety and cycle life. The low coulombic efficiency, unstable solid-electrolyte interphase, dendrite growth, and volume expansion of metal anodes limit their engineering development.

To address the abovementioned problems, the construction of an artificial interface layer and optimization of the electrode structure can be conducted to improve the stability of the multi-electron metal anode interface, reduce the local current density, induce uniform electrochemical stripping and deposition on the metal anode, and buffer the effect of volume changes on safety. Moreover, the chemical properties of electrolytes have a major impact on the stability of multi-electron metal anodes. In addition, electrolyte composition optimization by constructing metal cation self-healing electrostatic shielding [12] and a targeted anchoring mechanism [13] can facilitate uniform deposition of metal ions on the anode surface, thereby fundamentally altering Li dendrite formation. Conversely, the nucleation and growth of metal cations depend on the working current density of the battery, and metal dendrite formation can be effectively suppressed under conditions of limited current density and discharge depth. Consequently, future engineering applications of multi-electron metal anodes should consider the application prospects of battery systems (Fig. 1 [3]).

3.4. Cost management of large-scale production

In addition to the electrochemical performance and safety characteristics of multi-electron battery systems, cost management plays an important role in their engineering application. Owing to the additional conductive agents, binders, and other auxiliary materials used in current commercial lithium-ion batteries, lithium metal anodes have a theoretically lower cost (36 $\text{USD}\cdot(\text{kA}\cdot\text{h})^{-1}$) than graphite anodes (70 $\text{USD}\cdot(\text{kA}\cdot\text{h})^{-1}$) [14]. Furthermore, the application of S, O₂ cathode materials with higher theoretical energy densities in next-generation high-specific-energy battery systems can considerably reduce the total cost [5]. For large-scale integrated control, the standardization construction and large-scale production process of new technology, equipment, and materials should be expedited.

4. Discussion: Multi-electron battery system paths ahead

Various high-energy-density battery systems based on multi-electron reaction mechanisms, such as intercalation, anionic redox, conversion, and alloying reactions, have been developed. In particular, anionic redox reactions and conversion reactions are thought to be the most promising routes for multi-electron transfer in cathode electrode materials [3]. With the application of multi-electron cathodes and anodes, future advanced battery technologies could provide higher energy densities than commercial lithium-ion batteries. Consequently, metallic electrodes, silicon, and phosphorus are considered to be ideal anode materials. Transition metal oxides (TMO) based on anionic redox reactions (ARRs) can be used as high-energy-density cathodes with high technological maturity and a long cycle life. When these cathodes are assembled by alloying Si or P anodes, the full cells can provide a considerable energy density at high operating voltages. Si anodes are now widely used in commercial lithium-ion batteries with an energy density of $300 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$ due to their high theoretical specific capacity ($4200 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$). However, the key technical problems associated with electrochemical cycling, such as large volume expansion, low conductivity, and poor cycling performance, must be addressed through carbon coating, nano-sized Si, and active/inactive alloys. Li metal possesses a high specific capacity ($3861 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$) and an ultra-low chemical potential (-3.041 V versus a standard hydrogen electrode). If a Li metal anode is applied to a next-generation multi-electron battery system, the actual energy density can exceed $400 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$, thereby meeting the growing demand for high-energy-density, long-cycle-life, and

low-cost batteries. Consequently, it is necessary to adjust the deposition behavior of Li through interface modification and structural design to inhibit Li dendrites and slow the breakdown of Li anodes.

Lithium-rich oxides based on ARR exhibit approximately twice the capacity of traditional lithium-ion battery cathode materials, including LiCoO_2 , $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, and LiFePO_4 , because the anions, in addition to transition metal cations, participate in multi-electron transfer during the electrochemical reaction process. Sulfur molecules can provide 16 electron transfers in the electrochemical reaction, which contributes to a high theoretical specific capacity of $1675 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ [15]. Li-S and Li-O₂ batteries are expected to be applied as the next generation of energy storage technology, with an extremely high theoretical energy density of more than $2600 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$ (Fig. 2) [16].

Currently, Li-S batteries face the challenges of a mismatched interface, shuttle effect, insulating properties, and Li-O₂ batteries, which correspond to slow oxygen reduction reaction (ORR)/oxygen evolution reaction (OER) dynamics, unstable O₂ intermediates, and parasitic reactions. These can be optimized by interface engineering, functional additives, and catalyst design in engineering applications. Additionally, solid-electrolyte-based multi-electron battery systems matched with lithium metal anodes and multi-electron positive electrodes are considered to be the most promising devices for energy storage because of their inherent safety and potentially high energy density. However, because these multi-electron transfer reactions are usually conducted at high operating voltages, the instability of the electrode structures and electrolytes is a major barrier and requires further research on the electrolytes, interface stability, and solvated ions.

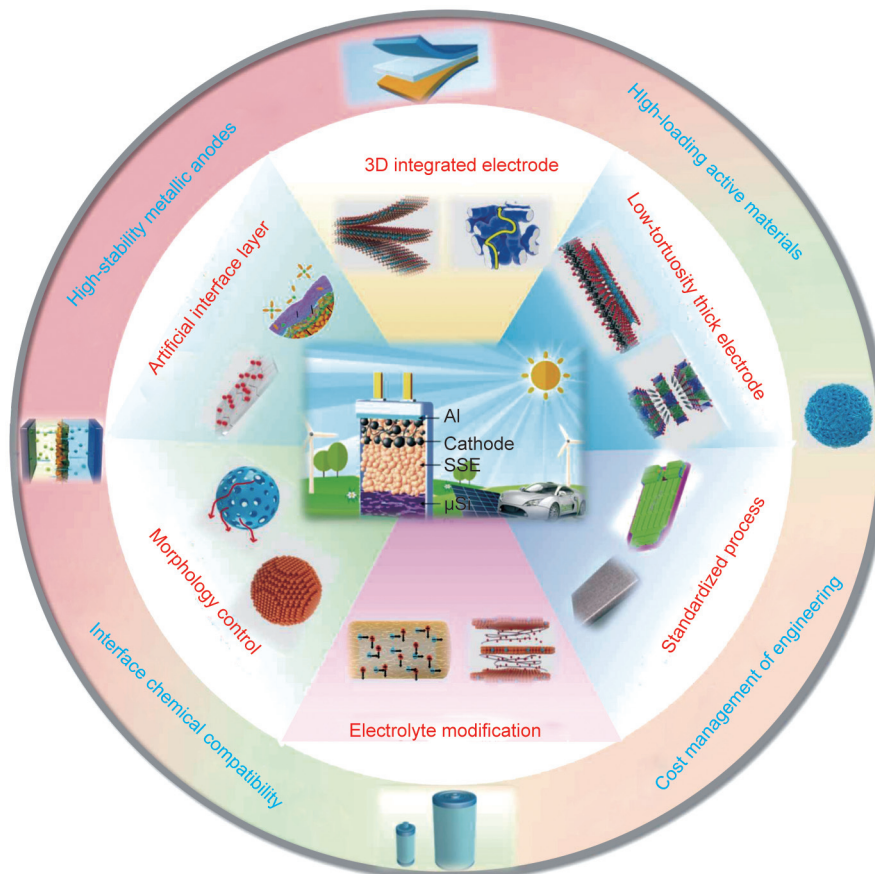


Fig. 1. Schematic of the engineering development of a multi-electron battery system. Reproduce from Ref. [3] with permission. SSE: solid-state electrolyte; μSi : micro-sized Si.

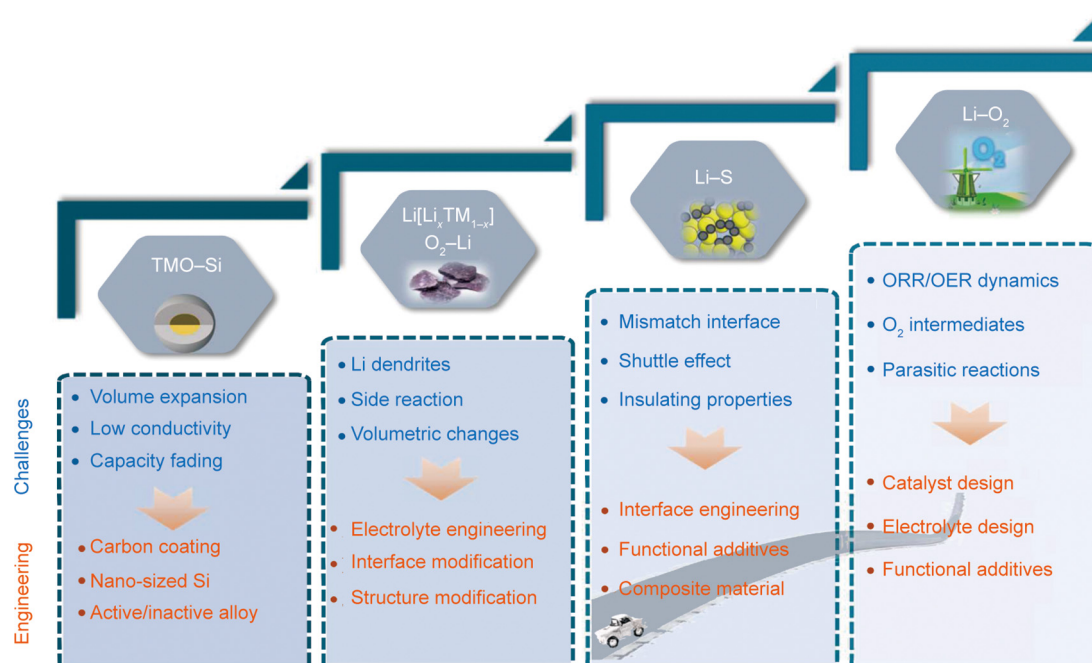


Fig. 2. Schematic of the routes ahead for multi-electron battery systems. TMO: transition metal oxides; TM: transition metal; ORR: oxygen reduction reaction; OER: oxygen evolution reaction.

5. Conclusions

Multi-electronic reaction mechanisms have created the most effective solutions for new-style battery systems with a long cycle life, high safety, and low cost for future electric vehicle power demands. Light, and multi-electron reaction-mechanism-based advanced battery systems challenge the single-electron reaction theory and broaden the scope of battery material research. Furthermore, a considerable improvement in energy density through a multivariate synergy strategy can accelerate the innovation and development of new high-performance battery systems in the clean energy industry.

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