

Beyond Lithium-Ion Batteries

Exploring the Latest Advancements in Battery Materials and Characterization Techniques



Introduction

Rechargeable lithium-ion batteries (LIBs), commercially pioneered 33 years ago, have emerged as the preferred power source for portable electric devices, electric vehicles (EVs), and LIBs-based grid storage systems. Despite their high electromotive force, lightweight design, and impressive energy

density, there is an urgent need to reduce costs, enhance safety, and increase energy density, especially for EVs. The demand for lower costs, enhanced safety, resource sustainability, and higher energy density has propelled the research and development of "beyond Li-ion" battery technologies.

Battery Technologies

Various "beyond Li-ion" battery technologies are being explored to meet the growing demands for sustainable energy storage solutions.



Sodium-Ion Batteries

Sodium-ion batteries (NIBs) have emerged as a strong contender due to the abundance and low cost of sodium. These batteries operate similarly to lithium-ion batteries but use sodium ions as charge carriers.¹

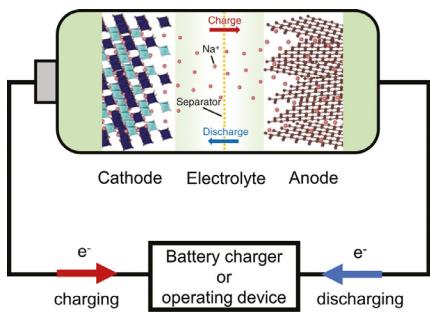
Advantages:

- Abundant and inexpensive raw materials.
- Potential for high energy density.
- Environmental benefits.

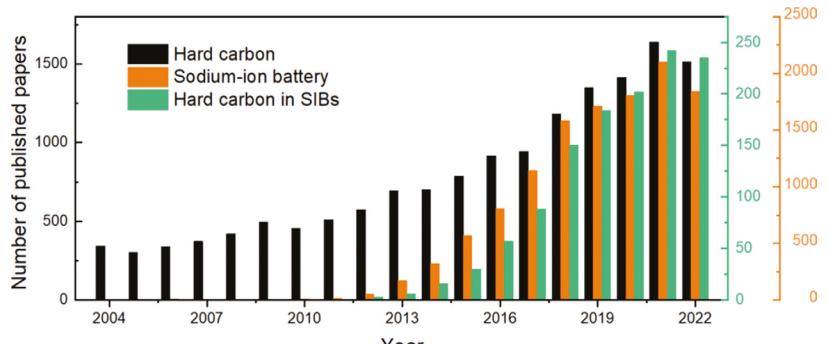
Challenges:

- Lower energy density compared to lithium-ion batteries.
- Limited cycle life and stability issues.

Working principle of NIB



Graph showing number of published papers





Potassium-Ion Batteries (PIBs)

Recently, potassium ion batteries have gained more attention due to the high earth-abundance and low cost of K.²

⊕ Advantages:

- Potassium is abundant and inexpensive, making PIBs a cost-effective alternative to LIBs.
- **High Energy Potential:** Due to potassium's low redox potential (-2.92 V), PIBs can offer high energy densities.

⊖ Challenges:

- **Larger Ionic Radius:** The larger ionic radius of K⁺ (1.38 Å) compared to Li⁺ (0.76 Å) causes structural instability in electrodes and sluggish reaction kinetics, leading to poor cyclic stability.
- **Need for Suitable Electrode Materials:** Identifying and developing the most suitable electrode materials for PIBs is crucial to overcoming these challenges.
- **Energy-Intensive Preparation:** Most doping processes for carbon materials involve high energy consumption or complex procedures, hindering large-scale utilization.
- **Synergistic Effects:** The combined effects of heteroatom doping and topological structure are not well understood, complicating the determination of electrochemical performance.



Innovative Solutions

- **Amorphous Carbon with Hollow Structures:** These materials provide more active storage sites, improved interfacial wettability, and reduced diffusion paths for ions and electrons, enhancing specific capacity and rate performance.
- **Heteroatom Doping:** Doping carbon materials with elements like N, S, and P can create surface defects and active sites, enhancing K-ion adsorption and improving electronic conductivity and interlayer distance.



Solid-State Batteries

Solid-state batteries (SSBs) replace the liquid electrolyte with a solid electrolyte, offering significant safety and performance advantages. These batteries promise higher energy density and enhanced safety.³

⊕ Advantages:

- Improved safety (non-flammable).
- Higher energy density.
- Longer cycle life.

⊖ Challenges:

- Manufacturing complexity.
- High production costs.
- Interface stability issues.



Aqueous Zinc Ion Batteries (AZIBs)⁴

⊕ Advantages:

- **Abundant Zinc:** Zinc is plentiful and widely available, reducing material costs.
- **Low Cost:** Overall, AZIBs are cost-effective compared to other battery technologies.
- **High Ionic Conductivity:** The aqueous electrolyte provides high ionic conductivity, which enhances battery performance.
- **Reduced Safety Risks:** The use of aqueous electrolytes minimizes safety risks associated with flammable organic solvents.

⊖ Challenges:

- **Electrolyte Compatibility:** Initial development faced issues with chemical and electrochemical compatibility between the electrolyte and Zn electrodes.
- **Narrow Voltage Window:** The working voltage window of AZIBs is limited, affecting their overall efficiency.
- **Zn Dendrite Formation:** Poor reversible Zn plating/stripping and the formation of Zn dendrites lead to low Coulombic efficiency (CE).
- **Irreversible Byproducts:** Formation of byproducts such as ZnO and Zn(OH)₂ in alkaline environments hinders battery performance.
- **Cathode Material Stability:** Cathode materials must be stable at high voltage and provide large capacity, which is challenging to achieve.
- **Rate Performance:** Significant rate performance and gravimetric power density require high ionic/electronic transport and sufficient redox reaction kinetics.
- **Cycling Stability:** Good cycling stability depends on the structural integrity and stability of cathode materials.
- **Material Compatibility:** Despite advancements, many cathode materials like Prussian blue analogues, vanadium-based materials, Chevrel phase compounds, and organic compounds do not exhibit sufficient electrochemical performance for commercialization.
- **Performance Interpretation:** Difficulty in rigorously interpreting performance results highlights the need for more systematic methods in evaluating cathode materials.
- **Design Strategies:** Necessary design strategies for Zn anodes and electrolytes need to be established to match with cathode materials for commercialization.

Practical Challenges

Potential Strategies

AZIBs
Cathodes

Matched Anode/Electrolyte



Na-S

Sodium-Sulfur (Na-S) Batteries

Room-temperature sodium-sulfur (RT Na-S) batteries have emerged as a promising candidate for next-generation scalable energy storage systems, due to their high theoretical energy density, low cost, and natural abundance.⁵

Advantages:

- High Energy Density:** Na-S batteries provide high energy density, making them suitable for large-scale energy storage.
- Cost-Effectiveness:** They are low-cost compared to other battery technologies, which is crucial for large-scale applications.
- Flexibility:** These batteries can be used for both power-type and energy-type energy storage, offering versatility in their applications.
- Environmental Impact:** Na-S batteries support carbon peaking and carbon neutrality initiatives, contributing to global efforts to combat climate change.
- Commercial Prospects:** Room-temperature (RT) Na-S batteries have promising commercial prospects due to their lower operational costs and reduced safety hazards compared to high-temperature (HT) Na-S batteries.

Challenges:

- High Operational Costs and Safety Issues:** HT Na-S batteries operate at high temperatures (300–350 °C), leading to significant running costs and safety concerns.
- Volume Expansion:** The S cathode undergoes a 170% volume expansion upon conversion to Na₂S, which can destroy the cathode structure and cause active material loss and rapid capacity decay.
- Poor Electrical Conductivity:** Sulfur and its intermediates (Na₂S₂ and Na₂S) have poor electrical conductivity, resulting in sluggish reaction kinetics.
- Shuttling Effect:** In ether-based electrolytes, the dissolution of long-chain NaPSs leads to active material loss, Na anode corrosion, and low Coulombic efficiency.
- Side Reactions:** In carbonate-based electrolytes, side reactions between NaPSs and carbonate solvents occur due to high nucleophilic activity.
- Na Dendrite Growth:** Uncontrolled proliferation of Na dendrites during extended cycling can cause an uneven Na metal surface, reducing Coulombic efficiency and posing safety risks such as short-circuits and thermal runaways.
- Cost of Sodium:** Securing a cost-effective source of metal sodium is essential for large-scale energy storage applications.

Outlook: Emerging Technologies

Beyond sodium-ion and solid-state batteries, several emerging technologies are being explored, including magnesium-ion, aluminum-ion, and zinc-air batteries. Each offers unique advantages and challenges.

Magnesium-Ion Batteries:

 High volumetric capacity.

 Stable electrode materials.

Aluminum-Ion Batteries:

 High charge storage capacity.

 Abundant raw materials.

Zinc-Air Batteries:

 High energy density.

 Low cost and environmentally friendly.

Conclusion

The quest for the ideal battery technology continues, with each alternative offering unique benefits and facing distinct challenges. Ongoing research and innovation are essential to unlocking the full potential of these promising energy storage solutions.

Further Reading

Explore our latest eBooks on cutting-edge battery technology:

1. <https://advancedopticalmetrology.com/electronics/ebook-17-lithium-ion-batteries.html>
2. <https://advancedopticalmetrology.com/batteries/ebook20-exploring-advanced-battery-technologies-powering-the-future.html>
3. <https://advancedopticalmetrology.com/batteries/dendrite-free-zn-ion-battery-performance.html>

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<https://doi.org/10.1002/adfm.202302277>

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<https://doi.org/10.1002/adfm.202301987>

3. Y. Dong *et al.*, Solid-State Electrolytes for Sodium Metal Batteries: Recent Status and Future Opportunities. *Adv. Funct. Mater.* 2024, 34, 2213584.

<https://doi.org/10.1002/adfm.202213584>

4. G. Li *et al.*, Developing Cathode Materials for Aqueous Zinc Ion Batteries: Challenges and Practical Prospects. *Adv. Funct. Mater.* 2024, 34, 2301291.

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5. Source: Y. Liu *et al.*, Recent Advances in Transition-Metal-Based Catalytic Material for Room-Temperature Sodium–Sulfur Batteries. *Adv. Funct. Mater.* 2024, 34, 2302626.

<https://doi.org/10.1002/adfm.202302626>

Published by

WILEY

This infographic is based on:

Advanced Functional Materials: Volume 34, Issue 5; Special Issue: *Beyond Lithium-Ion Batteries*, January 29, 2024