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Special Collection

Batteries & Supercaps: Beyond Lithium-Ion Batteries

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It was about thirty years ago, with the first successful commercialization of lithium-ion batteries (LIBs), that a new era begun. These new electrochemical energy storage systems were about to transform the way society communicates, moves, and lives. The journey that led to this success started back in the early 70s until the mid 1980 paving the way for LIBs commercialization in 1991.[1] LIBs undoubtably represent the most successful example of secondary battery. Their importance is reflected in the 2019 Nobel Prize for Chemistry awarded to Dr. Yoshino, Prof. Whittingham, and Prof. Goodenough for their pioneering work toward the development of the LIB technology.[2]

In the years following commercialization, the performance of LIBs has drastically improved until 1995, when the golden combination was achieved by matching graphite at the anode, $LiCoO_2$ at the cathode, and a carbonate-based solution as the electrolyte.[3,4] In the last two decades, the Li-ion technology based on intercalation chemistry has seen tremendous technological improvements. This success has been achieved through extensive collaborative teamwork across the world, involving research and development on a variety of disciplines at the interface between chemistry, material science, engineering, and physics. Continuous improvement of the cell technology has been achieved by combining efforts in material optimization as well as advanced engineered cell manufacturing processes. Nowadays lithium-ion cells are lighter, smaller, cheaper, and safer while exhibiting improved energy and power density.[5]

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Driven by the societal and governmental goals of transitioning to a low-carbon economy, the continuously growing global battery demand will approach 1,000 GWh in 2025. The main contributor to the rising demand for LIBs is the electric vehicle (EV) market. The stationary storage market is also expected to experience significant growth in the next decades.[5] The global demand is growing at a very fast pace and calls for improved cell technologies able to satisfy a variety of requirements according to the final application. Market diversification and different application requirements accelerate the research toward the next-generation electrochemical energy storage systems, including sodium-based batteries and multivalent chemistries, where safety, cost, sustainability, dependency on raw critical materials, and manufacturability are critical parameters to be considered. In such a scenario, beyond LIB technologies, including supercapacitors and hybrid systems, may play a crucial role and become the next generation sustainable electrochemical energy storage system of the future.

This Special Collection aims to highlight the dynamic research environment surrounding electrochemical energy storage technologies bringing together the latest research conducted beyond lithium-ion batteries. Ten reviews and twelve articles highlight the vivid research efforts undertaken all over the world in a variety of different systems including Na-ion, K-ion batteries, Mg-, Ca-, Al-, Zn-based systems as well as all solid-state, dual-ion batteries, and hybrid batteries and supercapacitors.

A substantial amount of contributions are focused on the investigation of Na-based battery chemistries, highlighting the great interest and research efforts currently ongoing on these technologies. Indeed, in the last decade, the development of Na-ion and Na-based chemistries, including solid-state systems, Na–sulfur (Na/S) and Na–air (Na/O_2), has continuously grown. Na-based batteries have the potential to represent the next generation sustainable and low-cost energy storage solution. Great achievements in terms of materials development have been reported. However, further work is still needed to fully understand a proper structure-function correlation in several Na-ion battery materials. In this collection, two review papers report on the importance of a fundamental understanding of the thermodynamic and kinetic processes occurring upon sodiation and de-sodiation and their characterization for a rational design of functional and high-performance Na-battery materials. **Brennhagen et al.** discuss operando X-ray methods providing a critical summary of the characterization techniques that have been applied to Na-ion, Na/O_2, and Na/S batteries,

Editorial
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offering valuable insights on the choice of the cell design, data processing, and future opportunities. **Gotoh** reports on the use of solid state nuclear magnetic resonance (SS-NMR) as a powerful tool to obtain information on the sodiation mechanism of layered cathode and anode materials including carbon and inorganic compounds.

Among the Na-ion cathode candidates proposed so far, transition metal layered oxides and polyanionic compounds have certainly attracted large attention in the Na-ion battery community. In this Special Collection, **Peng et al.** highlight the importance of the particle morphology and crystal orientation on a Ni–Mn P2-type layered oxide cathode, proposing a one-pot synthesis method for high energy/high power applications. Also, in search for low-cost cathode candidates, **Fehse et al.** investigate the $Fe^{4+/3+}$ redox couple in $NaFeO_2$ by simultaneous operando nuclear resonance and X-ray scattering studies. **Lan et al.** study the ionic conductivity of $Na_3V_2P_3O_{12}$ (NVP) in an all-solid-state battery (ASSB) cell. It is found that the ionic conductivity decreases with increasing electrochemical potential, thus limiting high-rate cycling of the ASSB. The authors propose that small particle sizes are required in order to reduce the ohmic polarization and concentration polarization and increase the power density of Na-ASSBs.

Electrolyte is certainly a key player in all electrochemical systems. In this special collection, two review papers on this topic for Na batteries are presented. **Yu et al.** provide information on the transport of Na ions in solid electrolytes whereas **Hijazi et al.** focus on non-aqueous systems.

For the latter ones, one of the main challenges is to ensure the formation of a stable solid–electrolyte interphase (SEI) at the negative electrode. This crucial factor is assessed by **Moon et al.** by studying the differences in the SEI stability in Li and Na cells by using hard carbon electrodes. By tuning the

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Editorial
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electrolyte system and designing a composite Sn/graphite anode for Na-ion batteries, a Na hybrid supercapacitor is also presented by **Palaniselvam et al.**, providing insightful information on this type of high power device.

In their work, **Garcia-Quintana et al.** investigate hybrid electrolytes in Na–O_2 batteries, elucidating the role of speciation in glyme-ionic liquid hybrid systems. **Liang and Lu** provide insights into the mechanistic understanding of oxygen electrodes in metal–O_2 batteries, while **Chen et al.** provide an overview of the latest works focused on using in situ Raman and Fourier transform infrared spectroelectrochemical techniques for studying the electrode–electrolyte interface of Li–O_2 batteries.

Among the other monovalent systems, K-ion batteries have also attracted interest. In this special collection, **Verma et al.** summarize the most recent development on electrolyte systems for K-ion batteries while **Zhang et al.** shift the focus on carbon based anodes. From an application point of view, these systems might not result very appealing, especially when considering safety aspects. However, from a scientific point of view, they offer ideal comparative systems to evaluate the performance of Li and Na systems.

Multivalent-based ions battery (MIB) technologies are interesting post-Li electrochemical energy storage devices. Beside the promising properties, they are still at a very early stage of research. In this special collection, **Maroni et al.** provide a comprehensive review on Mg and Ca systems, highlighting also the difficult experimental conditions related to the electrolyte systems and the cathode materials required to investigate these systems. In addition, **Bitenc et al.** evaluate the electrochemical performance and mechanism of Ca metal-organic batteries while **Meister et al.** assess the use of Mg-based ionic liquid electrolytes for hybrid dual-ion capacitors.

Among the multivalent systems, Zn-based energy storage devices have received extensive attention in view of their low-cost and high-safety characteristics. Numerous breakthroughs have been made in this field in recent years. In this special collection, **Li and Hu** discuss a comprehensive overview of the recent progress on Zn metal energy storage devices under extreme conditions of low temperatures including the design of anti-freezing electrolytes, low-temperature-resistant cathode materials, and Zn anodes.

Al-graphite dual-ion batteries represent another compelling battery concept especially for large-scale stationary storage application in view of their safety, low-cost, long-cycling life, and high-energy efficiency. Two articles are reported on this topic with a focus on their electrolyte systems. **Wang et al.** study the $AlCl_3$-saturated ionic liquid anolyte with an excess of $AlCl_3$, while **Elia et al.** compare chloroaluminate melts.

Beside non-Li chemistries, in this special collection two further contributes on beyond lithium-ion systems are highlighted. **Touja et al.** discuss the use of metal anodes such as Li, Na, K and Mg. They propose metal electrode surface engineering strategies with a focus on the use of metal coatings forming alloys and their possible practical transfer to the battery industry.

The possible use of a solid-state system enabling Li metal use in combination with a sulfur cathode is also discussed by **Dewal et al.** Their work focuses on the analysis of charge carrier transport in an all-solid-state Li–S batteries.

This Special Collection groups together the latest research conducted toward the development of beyond lithium-ion battery technology. It is clear that the challenges faced by the systems are multifaceted. Indeed, the challenges to be tackled lie at the interface of chemistry, materials science, surface science, and engineering. A multidisciplinary approach is needed to understand the key interfaces, structures, and mechanisms relevant to these systems. No single technique can simultaneously achieve the chemical, structural, temporal, and spatial sensitivity required to understand all aspects. Multidisciplinary, international collaborations combining experimental and computational methods are required to unveil key knowledge and critical insights necessary for the development of the future battery technologies.

In conclusion, it has been a privilege to edit this Special Collection. We would like to particularly thank all the contributing authors for their great work and the reviewers for their commitment. A special **Virtual Symposium**, jointly organized by *Batteries & Supercaps* and *ChemElectroChem*, was also originated based on this project. Finally, we would like to thank Greta Heydenrych, Rosalba A. Rincón, and Kate Lawrence for initiating this Special Collection, handling all the papers, and coordinating the virtual symposium.

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