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In Charge of the World: Electrochemical Energy Storage

As the global demand for energy and the concerns of environmental pollution grow, clean, renewable energies like solar and wind are becoming appealing to replace the conventional energy platform based on fossil fuel. However, these renewable energy sources are intermittent; therefore, efficient storage of electricity produced by them is critical to deliver stable, consistent power to the consumer when needed. On the other hand, the increasing capabilities of portable electronic devices as well as the desire for long driving distances between recharges of electric vehicles require electrical energy storage (EES) systems with high energy density. Electrochemical energy storage technologies are the most promising for these needs,¹ but to meet the needs of different applications in terms of energy, power, cycle life, safety, and cost, different systems, such as lithium ion (Li ion) batteries, redox flow batteries, and supercapacitors, need be considered (Figure 1).



Figure 1. A schematic showing electrochemical energy storage (e.g., Li ion batteries, flow batteries, and supercapacitors) for different needs, supporting a greener earth.

Although these systems have common operating principles, they have different requirements on electrode and electrolyte materials. Significant advances in the basic understanding of the component materials and performance improvements have been made in recent years, but many challenges still remain to be overcome.

Li ion battery technology has evolved tremendously since its first commercial launch by Sony in 1991. Its success in powering portable electronics is largely due to the high operating voltages (~ 4 V) offered by the oxide cathodes developed by Goodenough.² However, the layered LiCoO_2 , which was used in the first generation of cells commercialized by Sony, has a limited capacity of $\sim 140 \text{ mA h g}^{-1}$ at 3.7 V.³ To increase the energy density further, the lithium-excess layered oxides $\text{Li}[\text{Li}_x\text{Mn}_{1-x}\text{Ni}_y\text{Co}_z]\text{O}_2$, which are solid solutions between layered $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ and LiMO_2 ($\text{M} = \text{Mn}, \text{Ni}, \text{Co}$), have

become appealing in recent years due to their high capacity values of $\sim 250 \text{ mA h g}^{-1}$.³ The high capacities of these oxides arise from the irreversible loss of oxygen from the lattice during first charge and the consequential lowering of the oxidation state of the transition-metal ions at the end of first discharge. However, these materials suffer from a few limitations, (i) huge irreversible capacity loss of 40–100 mA h g^{-1} in the first cycle due to the elimination of part of the oxide ion and lithium ion vacancies from the layered lattice at the end of first charge, (ii) poor rate capability arising from the low electronic conductivity of localized Mn^{4+} ions and insulating surface layers formed by the reaction of the cathode surface with the electrolyte at the high operating voltage of ~ 4.7 V, and (iii) voltage fade during cycling due to the transformation of the layered phase into a spinel-like phase.

In a Perspective of this issue, Yu and Zhou first discuss the pristine structure of the lithium-excess layered oxides based on the average and local structure analysis, indicating two possible structures — two phases or a homogeneous solid solution — for these oxides (Yu, H.; Zhou, H. High-Energy Cathode Materials (Li_2MnO_3 – LiMO_2) for Lithium-Ion Batteries. *J. Phys. Chem. Lett.* 2013, 4, 1268–1280). They also discuss the reaction mechanism of the lithium-excess layered oxides, pointing out that a new phase (MnO_2) is most likely formed during the first charge process above 4.4 V and transformed to a spinel-like framework during the following cycles based on the electrochemical data, dQ/dV curves and kinetic analysis. Further, they point out that the reaction mechanism associated with the mysterious anomalous capacity of these oxides at high temperature may be different from that occurring at room temperature. To overcome the problems and improve the electrochemical performance of lithium-excess layered oxides, a number of approaches such as new synthesis methods,^{4,5} surface treatment with metal oxides and phosphates,^{6,7} and doping⁸ have been pursued. However, the low initial Coulombic efficiency, low rate capability, and voltage instability during cycling prevent their adoption in practical Li ion batteries.

Redox flow batteries (RFBs) can store energy with two soluble redox species in external tanks instead of having two solid electrodes within the cell. The flow-through systems offer many advantages, such as independent variation of energy and power ratings, simplicity in cell and stack structures, and minimum internal resistance due to liquid electrolytes and their intimate interfacial contact with the electrodes.¹ These advantages make RFBs appealing for large stationary energy storage systems with capacities in the range of 1 kW h–10 MW h. A few types of RFBs, vanadium RFBs, polysulfide bromide RFBs, and uranium RFBs, have been developed. Other types of RFBs have only a flowing electrolyte on the cathode side and a solid metal electrode on the anode side, for example, zinc–bromine RFBs and the recently developed lithium-metal-based RFBs.⁹ Vanadium RFBs, utilizing vanadium ions in different

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oxidation states on both sides of the cells, were first successfully developed at the University of New South Wales in the 1980s.¹⁰ Although large-scale vanadium RFBs have been demonstrated, many issues such as high cost, reactant crossover, and limited cycle life hamper their wide deployment.

In a Perspective in this issue, Ding et al. provide a survey of the current understanding of vanadium RFBs from materials to stacks (Ding, C.; Zhang, H.; Li, X.; Liu, T.; Xing, F. Vanadium Flow Battery for Energy Storage: Prospects and Challenges. *J. Phys. Chem. Lett.* **2013**, *4*, 1281–1294). Membranes, electrolytes, and electrodes are the key components within the vanadium RFBs. The goal to improve these materials is to reduce the cost, increase the efficiency, and maintain a long cycle life. For membranes, alternative low-cost proton-conducting materials to replace Nafion membranes have been developed. Most of them show advantages of high ion selectivity, but they usually have limited chemical stability in the presence of the highly oxidative V^{5+} ions. Modified Nafion membranes with improved ion selectivity can offer good chemical stability, but still at a higher cost. With electrolytes, a key issue is the low solubility and instability of the hydrated V_2O_5 present in them upon cycling, which can result in a blocking of the electrodes and reduction of cell efficiency. To overcome this problem, organic or inorganic additives as stabilizing agents can be mixed with the electrolyte to stabilize the high concentration of reactant ions. One of the most prominent approaches developed by the group of Gary Yang at PNNL is to employ a chloride supporting electrolyte or sulfate–chloride mixed acid system forming a vanadium dinuclear $[V_2O_3 \cdot 4H_2O]^{4+}$ or a dinuclear chloro complex $[V_2O_3Cl \cdot 3H_2O]^{3+}$.¹¹ Electrode materials that are mostly carbon felt or carbon paper are also critical for high-performance vanadium RFBs. Many alternative materials such as carbon nanotubes and graphene oxides have also been developed.^{12,13} An effective electrode developed in our group is nitrogen-doped carbon nanotube/graphite felt that can significantly enhance the cell performance.¹⁴ In addition to the materials, Ding et al. also present the construction of flow cell stacks and associated mathematical modeling, uncovering the kinetics of the redox reactions.

Supercapacitors offer an energy storage option that is in between those of rechargeable batteries and capacitors. They offer lower energy than batteries but higher power with fast charge/discharge rates and a much longer cycle life than rechargeable batteries.¹⁵ Compared to the traditional capacitors, supercapacitors offer much higher capacitance and energy density, making them appealing for applications that require fast charge.¹⁶ They are often used in conjunction with batteries to overcome the energy limitations. Additionally, supercapacitors are relatively safer compared to lithium ion batteries due to their ability to be overcharged. However, severe self-discharge behavior and low energy density are still the major challenges.

Since its discovery in 2004, graphene has been overwhelmingly pursued for many applications due to its unique electronic, optical, thermal, and mechanical properties.¹⁷ Early graphene supercapacitors were developed in 2008.¹⁸ In a Perspective by Chen et al. in this issue, recent studies about graphene-based electrochemical capacitors are reviewed and highlighted, including the strategies for graphene electrode fabrication, design principals of electrode structures, and the relationship between graphene properties and supercapacitor performance (Chen, J.; Li, C.; Shi, G. Graphene Materials for

Electrochemical Capacitors. *J. Phys. Chem. Lett.* **2013**, *4*, 1244–1253). Large specific surface area and high conductivity are two of the key properties of graphene to construct high-performance supercapacitors. A graphene network with an oriented microstructure can further improve the rate performance of electrochemical capacitors. To obtain additional functions, graphene sheets can be easily incorporated into other carbon materials, conducting polymers, or inorganic compounds. Although the electrochemical performance of supercapacitors can be significantly enhanced by employing graphene-based electrodes, the cost for synthesizing single-layered graphene is still too high to be scaled up for mass manufacturing.

In conclusion, electrochemical energy storage is becoming a much more critical part of our daily life. Efficient utilization of the abundant, clean, renewable energies requires high-energy, high-power, long cycle life storage devices at an acceptable cost. Current batteries and supercapacitors are limited by severe electrode and electrolyte materials challenges, and breakthrough materials with significant improvements are needed to move the field forward. Materials that can facilitate multielectron transfer per atom can increase the energy density significantly. For example, cathodes like sulfur and oxygen and anodes like silicon have become appealing in this regard in recent years.^{19,20} To realize practically feasible electrochemical energy storage devices at an affordable cost to meet the needs of future applications, coordinated interdisciplinary research and development efforts involving material scientists, chemists, and engineers are needed to understand the materials from an atomic/molecular to macroscopic level with the aid of computational approaches and advanced characterization techniques. With the successful development and deployment of long-life, low-cost electrochemical energy storage devices, our society will become green and sustainable.

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Notes

Views expressed in this Guest Commentary are those of the authors and not necessarily the views of the ACS.

The authors declare no competing financial interest.

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