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Energy storage emerging: A perspective from the Joint Center for Energy Storage Research

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Energy storage is an integral part of modern society. A contemporary example is the lithium (Li)-ion battery, which enabled the launch of the personal electronics revolution in 1991 and the first commercial electric vehicles in 2010. Most recently, Li-ion batteries have expanded into the electricity grid to firm variable renewable generation, increasing the efficiency and effectiveness of transmission and distribution. Important applications continue to emerge including decarbonization of heavy-duty vehicles, rail, maritime shipping, and aviation and the growth of renewable electricity and storage on the grid. This perspective compares energy storage needs and priorities in 2010 with those now and those emerging over the next few decades. The diversity of demands for energy storage requires a diversity of purpose-built batteries designed to meet disparate applications. Advances in the frontier of battery research to achieve transformative performance spanning energy and power density, capacity, charge/discharge times, cost, lifetime, and safety are highlighted, along with strategic research refinements made by the Joint Center for Energy Storage Research (JCESR) and the broader community to accommodate the changing storage needs and priorities. Innovative experimental tools with higher spatial and temporal resolution, in situ and operando characterization, first-principles simulation, high throughput computation, machine learning, and artificial intelligence work collectively to reveal the origins of the electrochemical phenomena that enable new means of energy storage. This knowledge allows a constructionist approach to materials, chemistries, and architectures, where each atom or molecule plays a prescribed role in realizing batteries with unique performance profiles suitable for emergent demands.

energy storage | Joint Center for Energy Storage Research | batteries | transportation | grid

behind-the-meter storage is changing the character of the transmission and distribution grid. Perhaps most important in the long run, the increasing urgency of decarbonization to avoid the most serious consequences of climate change is affecting all aspects of society spanning energy, healthcare, and agriculture. Such profound changes in the established expectations and operating norms of the transportation and grid sectors dramatically alter their future trajectories and, consequently, the research and development frontiers of the technologies that enable those pathways.

The Energy Storage Landscape Since 2010

In 2010 the cost of lithium (Li)-ion battery packs, the state of the art in electrochemical energy storage, was about \$1,100/kWh (2), too high to be competitive with internal combustion engines for vehicles or diesel generators and gas turbines for the grid. Instead, focus was on developing Li-ion batteries to support the growth of personal electronics, which require relatively small storage capacities in limited volume and weight formats. High energy density was the primary performance requirement for a personally carriable device, with cost, charging time, and lifetime distant followers. Early electric vehicles, such as the Nissan Leaf introduced in Japan and the United States in 2010, began to change battery performance expectations, with capacity (for driving range), cost (for competitiveness), and charging time (for

The global energy system has experienced dramatic changes since 2010. Rapid decreases in the cost of wind and solar power generation and an even steeper decline in the cost of electricity storage (Fig. 1) have made renewable power plants increasingly competitive with conventional fossil alternatives. The emergence of electric vehicles promises to disrupt the traditional dependence on petrochemicals and to potentially transform personal mobility. The advent of distributed energy resources including rooftop solar, demand management, and

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Global benchmarks - PV, wind and batteries



Source: BloombergNEF. Note: The global benchmark is a country weighed-average using the latest annual capacity additions. The storage LCOE is reflective of a utility-scale Li-ion battery storage system running at a daily cycle and includes charging costs assumed to be 60% of whole sale base power price in each country.

Fig. 1. Global average levelized cost of electricity (LCOE) from solar photovoltaic (PV) cells, wind, and Li-ion batteries. Reproduced with permission from ref. 1.

convenience) the prioritized characteristics. In the same time frame, storage for the electricity grid began to emerge for a few niche applications (3, 4) such as frequency regulation, but high cost precluded widespread deployment without stacking multiple benefits provided by a single battery installation (5-7). A growing recognition of the need for decarbonization to avoid the worst consequences of climate change introduced a qualitatively new feature into the energy system: replacing immediate return on investment with decades-long deferral of returns from mitigated climate volatility that ultimately accrue to society at large rather than to the original investors. Conventional markets are not designed to deal with this feature. Preexisting technologies based on fossil fuels cannot provide decarbonization without significant added cost, such as for carbon capture, use, and sequestration. This creates an opportunity for new technologies such as renewable energy, electricity storage, and electric vehicles to compete for dominance in the carbon-constrained era, in tandem with fuelagnostic measures such as grid modernization, demand-side management, ride sharing, and connected self-driving vehicles.

Around this same time, the US Department of Energy (US DOE) established Energy Innovation Hubs to apply leadingedge science and technology at scale to the world's most pressing energy challenges. At the launch of the Joint Center for Energy Storage Research (JCESR) in 2012, Li-ion batteries had increased their energy density by a factor of 3 at the cell level and decreased their cost by a factor of 2 at the pack level since their commercialization in 1991 (2, 8). Even with these remarkable achievements, the energy density and cost of state-of-the-art Li-ion batteries could not support the electrification of transportation. Early all-electric automobiles such as the Nissan Leaf had a driving range of ~70 miles, too low for a typical driver's needs and not competitive with incumbent internal combustion engine technology (9). For the grid, the outlook was even bleaker, with the levelized cost of electricity from Li-ion batteries 10x, 8x, and 3 to $4\times$ that of combined cycle gas turbines, coal, and gas peaker plants, respectively (1, 10).

The Future Energy Storage Landscape

As the price of energy storage falls, deployment in new areas is increasingly attractive. Commercial battery pack costs have dropped from \$1,100/kWh (2) to \$156/kWh in 2020 (11), electric

vehicles are maturing into worthy competitors for gasoline cars (12), and new storage solutions are being regularly deployed in the electricity grid to firm growing shares of renewables. Increasing global recognition of climate urgency is motivating deep decarbonization efforts across the board, from personal cars to long-haul trucks, maritime shipping, and aviation and to a fully renewable electricity grid (13, 14). These deployments of electrochemical energy storage are only the beginning; far more pervasive and serious technology needs frustrate the transformations of transportation and the electricity grid to low- or no-carbon status (15, 16). These challenges and opportunities require a diversity of batteries for a diversity of uses. Regional passenger flight, for example, requires high power for takeoff and landing; specific energy of 800 Wh/kg or more for a 600-mile range (17); fast charging during brief on-ground stops for passenger unloading and loading; and, somewhat remarkably, little attention to capital cost because operational costs are the dominant expense for airlines. Aviation performance needs are distinct from those of electric vehicles or the electricity grid. A second example is longduration storage (tens to hundreds of hours of discharge at variable power) to back up consecutive overcast or calm days on a highpenetration renewable electricity grid-this need cannot be met by the 4- to 6-h discharge time of Li-ion batteries (16, 18). Maritime shipping, long-haul trucking, and long-distance rail have different sets of performance needs. This broad range of applications requires a variety of purpose-designed batteries to satisfy the specific portfolio of requirements for each application.

The steep decline in battery costs is often compared to the similarly precipitous drop in the cost of solar photovoltaic cells (Fig. 1), with the comment that batteries are 10 y behind solar (19). While insightful, this comparison overlooks a fundamental difference between the two technologies. Solar cells conform to a single basic dominant design, with silicon as the active photovoltaic element and encapsulation by transparent glasses to protect against the surrounding environment. This design serves a single purpose, generating electricity, which, in turn, supports a host of uses. Energy storage presents a different picture, where the range of battery uses requires many disparate battery designs. As such, alkaline primary batteries, secondary lead-acid and nickel metal hydride batteries, and many others all serve vital functions. Batteries for personal electric vehicles require capacities 10,000× greater than batteries for personal electronics, and batteries for the electricity grid require 1,000× to 10,000× greater capacity than for electric vehicles; maritime shipping and aviation needs for capacity may be similar or even higher. Unlike solar cells, batteries are on the cusp of diversification to meet a wide variety of performance needs in the transportation and electricity sectors (19).

A Decade of Battery Development

It was clear when the Nissan Leaf was introduced in 2010 that cost was a primary impediment to energy storage for both transportation and the grid and that energy density for driving range was critical for transportation. Moreover, energy density and cost are interconnected as higher energy density reduces materials needed for the same storage capacity, thus lowering the cost. Thus, these two performance metrics dominated the energy storage landscape. Accordingly, JCESR prioritized fivefold increases in energy density to 400 Wh/kg at the pack level and fivefold decreases in cost to \$100/kWh at the pack level for transportation and grid batteries. JCESR elected to pursue several different battery formats for applications, specifically flow batteries for the grid as their independent scaling of power and energy offered a pathway to large energy storage capacities with decreasing cost per kWh, and lithium-sulfur (Li-S), lithiumair (Li-O), and multivalent batteries for transportation for their high theoretical energy densities and low material costs.

APPLIED PHYSICAL SCIENCES

To achieve its cost and performance targets, JCESR embarked on a top-down, reductionist approach to battery science, translating system-level energy density and cost performance goals into materials-level performance targets using a comprehensive set of technoeconomic models (20–29). These material-level targets were then pursued with heavily integrated fundamental science coordinating simulation, synthesis, characterization, and design. Driven by battery-level performance goals, this approach led to meaningful advances in the science and engineering of several different storage platforms, including nonaqueous flow batteries and air-breathing aqueous sulfur flow batteries for the grid and Li-S, Li-O, and magnesium-ion (Mg-ion) batteries for transportation which are summarized below.

Electricity Grid: Redoxmers, Polymer Membranes, and Long-Duration Storage

Redox flow batteries are rechargeable electrochemical systems that hold promise for long-duration energy storage at the low system costs needed for economic viability. In a typical system, two redox active species, operating at different potentials, are dissolved in liquid electrolytes, which are stored in tanks and pumped through a power-converting electrochemical stack where they are oxidized and reduced to alternately charge and discharge the battery. As compared to conventional enclosed rechargeable batteries (e.g., Li-ion and lead-acid), redox flow batteries have several key advantages of particular relevance to grid storage including decoupled power and energy scaling, long operational lifetimes with deep discharge capabilities, simplified manufacturing, and improved safety characteristics. Historically, the materials set of choice have been inorganic redox couples (e.g., V, Fe, Cr, Zn, and Br) dissolved in aqueous electrolytes whose lower cell potentials and solubilities limit energy density and cost reduction potential. Indeed, early stage technoeconomic modeling of multihour energy storage for the grid showed flow batteries to be a viable technology platform for lowcost energy storage provided the appropriate redox couples and associated electrolytes were identified (24, 27). To this end, JCESR has pursued nonaqueous flow batteries which utilize dissolved or suspended redoxmers (redox active organic monomer, oligomers, polymers, and colloids) as charge-storing fluids (30-35). Nonaqueous electrolytes offer the opportunity for increased cell voltages due to wider windows of electrochemical stability and access to new electrochemical couples that are incompatible with aqueous electrolytes due to either low solubility, chemical incompatibility, or redox potentials outside the stability window.

The use of redoxmers provides several additional benefits. First, the solvated diameter of redoxmers is large enough to be screened by inexpensive size exclusion membranes, which is a major cost advantage compared to expensive (and often ineffective) ion-selective membranes employed in the majority of precommercial and commercial flow batteries (31, 33). Second, redoxmers are a versatile molecular platform: a wide variety of pendant groups can be attached to linear or cyclic carbon backbones, providing nearly endless opportunities to control relevant properties such as operating voltage, number of charges transferred per reaction, solubility, and stability (35, 36). Third, the polymer architecture offers a scaffold for integrating functional groups that impart responsive behavior such as selfreporting state of health and self-repairing degradation, potentially significantly extending the lifetime of redoxmers and the flow battery (37). The design space of redox active organic materials is rich, broad, and complex, offering a powerful toolbox, which is only beginning to be understood. To accelerate progress, JCESR has developed and advanced computational methods such as genomic calculations, machine learning, and quantitative structure-property relations to augment traditional discovery approaches (38, 39). Application of these methods, in combination with synthesis and experiment, have yielded a range of new organic candidate species, including cyclopropenium monomers and dimers with solubilities up to 1.6 M in select nonaqueous electrolytes (40) and an all-organic nonaqueous flow battery with a cell voltage of 3.2 V (41), (Fig. 2).

In tandem, JCESR introduced polymers of intrinsic microporosity (PIM) as a new class of nanoporous membranes capable of size-screening redoxmers in redox flow batteries and soluble linear chain polysulfide intermediates in Li-S batteries (33, 42– 45). A flexible platform, these polymer membranes can be functionalized to enable charge selectivity, in addition to size selectivity, by incorporating redox switchable moieties into the polymer structure, as shown in Fig. 3 (33, 44). These potentially inexpensive polymer membranes are now being commercialized by Sepion, Inc., a startup spun out by JCESR (46). For the interested reader, further discussions can be found in a special virtual issue of *Macromolecules* devoted to polymers and other macromolecules that advance the frontier of electrochemical storage devices including Li-ion, Li metal, Mg metal, and redox flow batteries as well as supercapacitors (47).

In a separate grid effort, JCESR identified the emerging need for inexpensive long-duration storage (16, 18) and sought to address it with an entirely new kind of flow battery, an air-breathing aqueous sulfur battery (48, 49). Targeting storage needs with discharge times of days to weeks to firm electricity delivery in grids with high fractions of variable wind and solar, this battery employs exceptionally low cost materials: sulfur, an abundant byproduct of oil refining, water, and oxygen drawn from air. This approach enables unprecedentedly low system costs for electrochemical energy storage, similar to those of pumped hydroelectric storage, but in a smaller footprint free of locational constraints. Form Energy Inc., a JCESR start-up, is pursuing commercialization of this and other long-duration battery concepts (50).

Redoxmer-based flow batteries, inexpensive size-selective polymeric membranes, and air-breathing aqueous sulfur flow batteries are fundamentally new innovations with the promise and versatility to potentially solve the critical challenges of cost, lifetime, and long-duration discharge for a decarbonized electricity grid. JCESR and others are actively pursuing materials, chemistries, and architectures that can best implement these advances.



Fig. 2. Capacity versus cycle number for bulk electrolysis cycling of the thioether-substituted cyclopropenium derivative 2-Me⁺, shown above. Pairing this monomer with an unoptimized organic negative electrolyte (*N*-alkylphthalimide 6) enabled the demonstration of a 3.2-V all-organic non-aqueous flow battery. Reprinted with permission from ref. 41. Copyright (2019) American Chemical Society.



Fig. 3. PIMs can be synthesized for size selection with adjustable pore sizes up to 1.5 nm and for adaptive charge selection by incorporating redox switchable monomers that acquire charge after reaction with redox-active species in solution. Reproduced with permission from ref. 44.

Transportation: Li-S, Li-O, and Multivalent Batteries

In contrast to flow batteries, the compact, energy-dense format of a Li-ion battery is ideal for transportation applications. As such, the question became, what battery couples can theoretically deliver more energy per kilogram for less cost? Li-S, Li-O, and multivalent batteries all potentially contend in this space. JCESR's technoeconomic modeling identified excess electrolyte in Li-S batteries as a significant contributor to the high cost and low energy density of this technology (21, 22). Large electrolyte to electrode ratios are a standard feature of Li-S cells, enabling longer lifetimes by compensating for the continuous loss of electrolyte to parasitic side reactions during cycling (51). JCESR explored sparingly solvating electrolytes where limited solubility of intermediate polysulfide products restricts the liquid-phase parasitic side reactions (21, 52). Computational and characterization studies of solvated polysulfides revealed clustering of polysulfide chains in solution, suggesting a new mechanism of Li cation mobility: exchange of Li cations from one chain/cluster to another (53). Studies of sparingly solvating electrolytes, in turn, revealed alternate pathways for the Li-S discharge reaction that proceed through the solid instead of the liquid (54-57), an attractive solution that, in a single stroke, eliminates the solvation, side reactions, and migration of the polysulfide intermediates.

Li-O batteries are attractive for their very high theoretical energy density but usually suffer from short cycle life and high sensitivity to moisture and CO_2 in untreated air, necessitating the use of high-purity O_2 (23). JCESR introduced a new approach enabling a true Li-air battery, based on two-dimensional (2D) MOS_2 positive electrodes that catalyze the Li-O discharge reaction, a Li₂CO₃ protective layer on the Li metal negative electrodes, and an ionic liquid electrolyte that acts as a cocatalyst with MOS_2 . At the laboratory scale, the cell chemistry cycles 700 times and operates in untreated air with typical moisture and CO_2 content. Density functional theory calculations reveal that exposed Mo orbitals at the edge of the MOS_2 2D cathode act as the catalyst, opening a promising new approach to potentially practical Li-air batteries (58).

Using the Materials Project (59), JCESR explored multivalention batteries using multiply charged cations such as Mg^{2+} , Ca^{2+} , and Zn²⁺ instead of singly charged Li⁺. Massive materials simulation mapped the landscape of multivalent working ions and associated electrode structures. Over 1,800 combinations of divalent (Mg²⁺, Ca²⁺, and Zn²⁺) and trivalent (Al³⁺) cations paired with positive electrodes based on sulfides, oxides, fluorides, and phosphates were simulated for their voltage, capacity, energy density, and ion mobility (60). This comprehensive survey, the first of its kind, revealed trends in electrochemical properties and established an initial set of guiding principles for materials selection (61). A number of promising positive electrodes for Mg²⁺ cations were identified, of which many were synthesized with several demonstrating intercalation of Mg^{2+} (62–69) (Fig. 4). Separately, JCESR experimentally demonstrated three new long-cycling divalent battery chemistries, Mg-Ti₂S₄ (66), Zn-MnO₂ (70), and Ca-MnFe(CN)₆ (71). Significant insight into the mechanism of Ca^{2+} stripping and plating (72), the atomic-level phenomena behind the overpotential and nucleation rates for metal stripping and plating (73), and demonstration of facile Ca^{2+} stripping and plating at room temperature (74) expose new directions and promise for Ca-ion batteries. The weak coordination of Mg^{2+} by electron-deficient anions such as TPFA⁻ (TPFA⁻ = [Al{OC(CF₃)₃}]⁻) was shown to be an effective rational design strategy for electrolytes that extends the electrochemical window of Mg salts, rendering them kinetically inert to Mg⁺-mediated reduction (75) and enabling Mg plating without decomposition (76).

High mobility of multivalent ions in host electrodes and solid-state electrolytes has long been questioned because their larger Coulomb interactions were thought to hinder their motion. JCESR used nudged elastic band theory (77–79) to extensively explore the mobility of multivalent ions in crystalline hosts, revealing favorable local site symmetries that can enable high mobility despite their larger Coulomb interactions. This discovery, first revealed in computer simulations, was confirmed by experimental NMR and electrochemical impedance spectroscopy (80). A new simulation approach, electrostatically estimating the migration barriers in intercalation hosts, allows high-throughput computation to explore ion mobility systematically in many families of crystalline electrodes (81).

Batteries for transportation face many challenges to decarbonize not only personal cars but also buses, long-haul freight trucking, rail, maritime shipping, and aviation. JCESR's innovations in sparing solvation and solid state reaction pathways in Li-S batteries; MoS₂ catalysts, ionic liquid electrolytes, and protective Li coatings for long-cycling Li-air batteries; and new positive electrodes that enable high mobility of multivalent cations introduce promising new directions for high-energy density batteries. Implementing these new directions requires acceleration



Fig. 4. Crystal structure of chemically magnesiated ζ -V₂O₅ derived from synchrotron-based X-ray diffraction and transmission electron microscopy. Mg resides in a pseudosquare-pyramidal site with a frustrated fivefold coordination. Reprinted from ref. 69, with permission from Elsevier.

of materials discovery through advances in computation, machine learning, and artificial intelligence and understanding the fundamental origins of electrochemical behavior by in situ and operando characterization. This new knowledge will enable the deliberate design of battery materials, chemistries, and architectures at the atomic and molecular level to produce targeted overall battery performance.

Next-Generation Organic Electrolytes: The Electrolyte Genome

The battery community uses only a few dozen of the thousands to hundreds of thousands of possible liquid organic electrolyte formulations. JCESR sought to address this challenge by introducing the Electrolyte Genome, which brings to organic electrolytes the power and versatility of computational materials design which, up until then, had been focused on crystalline materials. The Electrolyte Genome draws on a database of tens of thousands of organic molecules cataloging their electron affinity, ionization potential, and other properties computed from first-principles or molecular dynamics calculations (82). This extensive information base enables understanding the solvation structures, dynamics, and chemical reactions of monovalent and multivalent ions in liquid electrolytes and their desolvation phenomena at electrode interfaces. JCESR discovered, for example, that multivalent cations such as Mg^{2+} , Ca^{2+} , and Zn²⁺ often pair with anions, a behavior not seen in the solvation of monovalent cations such as Li⁺ (83). Furthermore, when Mg²⁺ transitions to Mg⁺ before depositing as Mg⁰, the intermediate monovalent state is extremely active and capable of cleaving anions such as TSFI⁻ (TSFI⁻ = $[(CF_3SO_2)_2N]^-$) and solvents such as sulfones, revealing a fatal electrolyte decomposition mechanism (84). However, in electrolytes containing Cl^- , Mg^{2+} near the electrode interface solvates as the complex $MgCl^+$ coordinated by a shell of solvent molecules. This shell adsorbs preferentially on the electrode surface, and MgCl⁺ desolvates to Mg⁰ at low energy, enabling plating without decomposition of anions or solvent molecules (85, 86). This work reveals the atomic and molecular mechanism of Mg stripping and plating and opens the door to deliberate atomic-level design of multivalent electrolytes (87).

Safety and High Energy Density: Solid-State Electrolytes and Alkali Metal Negative Electrodes

Replacing flammable organic liquid electrolytes with nonflammable solid-state electrolytes eliminates thermal runaway reactions, a primary safety concern of Li-ion batteries. Pairing solid-state electrolytes with pure alkali metal negative electrodes significantly increases energy density, due to the greater gravimetric capacity of these metals: 3,860 mAh/g for Li and 1,165 mAh/g for Na versus 372 mAh/g for conventional graphite negative electrodes in Li-ion batteries. Na negative electrodes are attractive for the natural abundance and low cost of Na, should Li supply chains become strained by high battery demand for transportation and grid applications (88-90). The safety and energy density advantages of solidstate electrolytes and alkali metal negative electrodes make them an appealing target for rapid deployment. However, the high reactivity of Li and Na with most solid-state electrolytes creates spontaneous interfacial layers that often consume the alkali working ions and create interphases that block their transfer between electrolyte and electrode on charging or discharging (91-93).

JCESR introduced an inverse design strategy employing firstprinciples reactivity calculations to identify hydrates as reactants that spontaneously generate protective coatings for pure Na negative electrodes on contact with the solid-state electrolyte Na₃SbS₄. These coatings passivate the interface between Na negative electrode and solid-state electrolyte against further electrolyte reactions with Na and are permeable to Na cations but not to electrons. Hydrates form naturally on Na₃SbS₄ surfaces on exposure to air. Synchrotron X-ray depth profiling confirmed the first-principles reactivity predictions,

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opening a new route for rational design of practical solid state electrolyte interfaces (94).

In a separate surface science-based approach, thin films of Li are sputtered onto single crystal and polycrystalline surfaces of model (SrTiO₃) and real (LLZO) solid-state electrolytes, which are then characterized by X-ray photoelectron spectroscopy, atomic force microscopy, and X-ray absorption spectroscopy combined with density functional theory calculations (95, 96). Specific chemical reactions at the interface are observed, including the surprising roles of the crystallographic orientation and surface morphology of the solid electrolyte on the interfacial reaction sequence. This new Li sputtering approach exposes the normally buried interface between Li negative electrode and solid-state electrolyte to extensive multimodal characterization. In a third effort, JCESR spun out the startup company Blue Current to pursue development of polymer-based solid state electrolytes based on JCESR discoveries (97).

Exposing the normally buried interface between the electrode and the solid-state electrolyte to multimodal characterization and using first-principles reactivity calculations to predict spontaneously formed interfacial protective coatings represent two entirely new directions for understanding and implementing a wide range of solid-state electrolyte–metal electrode pairs. Their use by JCESR and the battery community will significantly accelerate progress in this important area.

The Current Challenge

The challenge of meeting varied cost and performance metrics for multiple distinct applications with a single battery technology is qualitatively illustrated in Fig. 5. Specifically, the disparity in energy storage requirements for two different scenarios, a battery in an electric vehicle (A in Fig. 5) and a battery for stationary energy storage (B in Fig. 5), is shown. A single system cannot be adapted to meet both sets of requirements. Intrinsic features of enclosed batteries (e.g., Li-ion batteries), for example, prevent full decoupling of energy from power, so that extremes of high energy/low power and low energy/high power are largely out of reach. Instead, we need a diverse set of battery platforms each specifically designed for a class of applications. Even for a single application, Li-ion batteries regularly fail to meet all of the



Fig. 5. Select performance and cost priorities for two hypothetical battery applications (i.e., A, electric car transportation; B, battery storing solar or wind energy for the grid). These distinct applications need separate purpose-designed batteries. Even for a single application, batteries typically cannot meet all of the performance needs simultaneously. These two challenges—a diversity of batteries for a diversity of uses and meeting all of the performance requirements for a given application—are the frontier of energy storage research.



Fig. 6. JCESR pursues transformative materials, chemistries, and architectures designed at the atomic and molecular level and built from the bottom up, atom by atom and molecule by molecule, where each atom or molecule plays a prescribed role in enabling targeted overall performance. These transformative materials, chemistries, and architectures can be mixed and matched to purpose-design batteries for current and future applications.

(often competing) performance requirements such as frequent cycling and long life, high energy density and low cost, or fast charging and no safety risk. The need for a diversity of battery platforms beyond the current technology and the inability of existing technologies to meet all of the required performance metrics for a given application are the two biggest challenges for energy storage. The state of the art of battery technology in meeting these two challenges is documented in the Factual Document (98) and Workshop Report (99) of the Basic Research Needs Workshop on Next Generation Electrical Energy Storage. The strategy and operation of JCESR is structured to address these two challenges.

The diversification of batteries to meet new application requirements implies new battery materials, chemistries, and architectures, some of which will deviate significantly from the conventional Li-ion format. This deviation will interrupt the long, steady decline in Li-ion battery costs (Fig. 1), which is due to 1) continuous incremental improvement in Li-ion positive electrodes and other materials and 2) an extended learning curve of continuous refinement of the manufacturing process supported by long-term growth of demand and production. Some of the materials advances now in the research phase, such as solidstate electrolytes and alkali metal anodes, promise significant

- V. Henze, Battery power's latest plunge in costs threatens coal, gas. (2019). https:// about.bnef.com/blog/battery-powers-latest-plunge-costs-threatens-coal-gas/. Accessed 2 April 2020.
- L. Goldie-Scot, A behind the scenes take on lithium-ion battery prices. (2019) https:// about.bnef.com/blog/behind-scenes-take-lithium-ion-battery-prices/. Accessed 2 April 2020.
- P. Denholm et al., The Value of Energy Storage for Grid Applications (National Renewable Energy Laboratory, 2013).

performance improvements as drop-in replacements that maintain the basic architecture and many of the manufacturing processes of conventional Li-ion batteries. Other battery advances, such as high-specific energy batteries for regional aviation or airbreathing aqueous sulfur flow batteries for long duration storage, will require new architectures and manufacturing processes that will increase costs, at least initially. In some cases, the higher manufacturing costs may be offset by lower materials costs and by supply chains that are more reliable and less complicated than for Li-ion batteries (89, 90). Game-changing batteries for applications with large market demand will benefit from long learning curves that will lower costs. Despite higher near-term manufacturing costs, these batteries may ultimately compete successfully with incumbent fossil technologies, just as solar panels and Li-ion batteries have done over the past decade.

To address the broad landscape of emerging and future energy storage applications, JCESR turned from its former top-down approach pursuing specific battery systems with high energy density and low cost to a bottom-up approach pursuing transformative materials, chemistries, and architectures that can be mixed and matched to produce batteries with a variety of targeted performance metrics spanning energy density, power, capacity, charge/discharge times, cost, lifetime, and safety. This range of performance metrics is needed to meet the needs of, for example, regional electric aviation, long-duration storage for backing up renewable generation on consecutive overcast or calm days, heavy-duty long-haul trucking, maritime shipping, long-distance rail, and hybrid use with fossil fuel in the short term and hydrogen fuel cells in the long term. Batteries suitable for many of these applications have yet to fully emerge.

JCESR pursues transformative materials, chemistries, and architectures by understanding and building batteries from the bottom up, atom by atom and molecule by molecule, where every atom and molecule plays a defined role in producing targeted system attributes, as illustrated in Fig. 6. This bottom-up approach, where battery-level performance is designed at the atomic and molecular level, is relatively new to battery research and development. This could not have been done 10 y ago, because our knowledge of the atomic and molecular origins of electrochemical phenomena was not sufficiently well developed. Modern tools such as in situ characterization, scanning electrochemical microscopy, coherent high-intensity X-ray beams that can access buried interfaces, computational simulation of electrochemical materials and phenomena, and artificial intelligence applied to materials discovery are rapidly building the knowledge base needed for this constructionist approach. The promise of bottom-up electrochemical design is significant acceleration of the pace of discovery and innovation by eliminating time-consuming trial and error that is often the backbone of battery research and development. JCESR aims to be on the frontier of bottom-up, atomic, and molecular-level design for next-generation batteries.

Data Availability Statement

There are no data associated with this manuscript.

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- D. Stenclik, P. Denholm, B. R. Chalamala, The role of energy storage for renewable integration. *IEEE Power and Energy* 15, 31–39 (2017).
- J. Eyer, G. Corey, Energy storage for the electricity grid: Benefits and market potential assessment guide, Sandia Report SAND2010-0815 (2010). https://www.sandia.gov/essssl/publications/SAND2010-0815.pdf. Accessed 2 April 2020.
- R. Hledik, R. Lueken, C. McIntyre, H. Bishop, Stacked benefits: Comprehensively valuing battery storage in California. http://files.brattle.com/files/7208_stacked_benefits_-_final_ report.pdf. Accessed 12 May 2020.

- 7. I. Staffell, M. Rustomji, Maximising the value of electricity storage. J. Energy Storage 8. 212-225 (2016).
- 8. G. Crabtree, E. Kocs, L. Trahey, The energy-storage frontier: Lithium-ion batteries and beyond, MRS Bull, 40, 1067-1078 (2015).
- 9. B. Howard, Will high-mileage Nissan Leafs need costly battery replacements soon? (2012). https://www.extremetech.com/extreme/136894-will-high-mileage-nissan-leafsneed-costly-battery-replacements-soon. Accessed 7 April 2020.
- 10. Anonymous, Lazard Levelized cost of energy analysis Version 13.0 (2019). https:// www.lazard.com/media/451086/lazards-levelized-cost-of-energy-version-130-vf.pdf. Accessed 2 April 2020.
- 11. M. Holland, Powering the EV revolution—Battery packs now at \$156/kWh, 13% lower than 2018, finds BNEF. (2019) https://cleantechnica.com/2019/12/04/powering-theev-revolution-battery-packs-now-at-156-kwh-13-lower-than-2018-finds-bnef/. Accessed 2 April 2020.
- 12. G. Crabtree, The coming electric vehicle transformation. Science 366, 422-424 (2019).
- 13. J. D. Jenkins, M. Luke, S. Thernstrom, Getting to zero carbon emissions in the electric power sector. Joule 2, 2498-2510 (2018).
- 14. M. Victoria, K. Zhu, T. Brown, G. B. Andresen, M. Greiner, The role of storage technologies throughout the decarbonisation of the sector-coupled European energy system. Energ. Convers. Manage. 201, 111977 (2019).
- 15. M. Arbabzadeh, R. Sioshansi, J. X. Johnson, G. A. Keoleian, The role of energy storage in deep decarbonization of electricity production. Nat. Commun. 10, 3413 (2019).
- 16. M. S. Ziegler et al., Storage requirements and costs of shaping renewable energy toward grid decarbonization. Joule 3, 2134-2153 (2019).
- 17. A. W. Schafer et al., Technological, economic and environmental prospects of allelectric aircraft. Nat. Energy 4, 160-166 (2019).
- 18. P. Albertus, J. S. Manser, S. Litzelman, Long-duration electricity storage applications, economics, and technologies. Joule 4, 21-32 (2020).
- 19. C. Bloch, J. Newcomb, S. Shiledar, M. Tyson, Breakthrough batteries-Powering the era of clean electrification. (2019). https://rmi.org/insight/breakthrough-batteries/. Accessed 2 April 2020.
- 20. J. D. Milshtein, R. M. Darling, J. Drake, M. L. Perry, F. R. Brushett, The critical role of supporting electrolyte selection on flow battery cost. J. Electrochem. Soc. 164, A3883-A3895 (2017).
- 21. L. Cheng et al., Sparingly solvating electrolytes for high energy density lithium-sulfur batteries. ACS Energy Lett. 1, 503-509 (2016).
- 22. D. Eroglu, K. R. Zavadil, K. G. Gallagher, Critical link between materials chemistry and cell-level design for high energy density and low cost lithium-sulfur transportation battery. J. Electrochem. Soc. 162, A982-A990 (2015).
- 23. K. G. Gallagher et al., Quantifying the promise of lithium-air batteries for electric vehicles. Energy Environ. Sci. 7, 1555-1563 (2014).
- 24. R. M. Darling, K. G. Gallagher, J. A. Kowalski, S. Ha, F. R. Brushett, Pathways to lowcost electrochemical energy storage: A comparison of aqueous and nonaqueous flow batteries. Energy Environ. Sci. 7, 3459-3477 (2014).
- 25. S. Ha, K. G. Gallagher, Estimating the system price of redox flow batteries for grid storage. J. Power Sources 296, 122-132 (2015).
- 26. R. Darling, K. Gallagher, W. Xie, L. Su, F. Brushett, Transport property requirements for flow battery separators. J. Electrochem. Soc. 163, A5029-A5040 (2016).
- 27. R. Dmello, J. D. Milshtein, F. R. Brushett, K. C. Smith, Cost-driven materials selection criteria for redox flow battery electrolytes, J. Power Sources 330, 261-272 (2016).
- 28. S. M. Laramie, J. D. Milshtein, T. M. Breault, F. R. Brushett, L. T. Thompson, Performance and cost characteristics of multi-electron transfer, common ion exchange nonaqueous redox flow batteries. J. Power Sources 327, 681-692 (2016).
- 29. V. Dieterich et al., Estimating the cost of organic battery active materials: A case study on anthraguinone disulfonic acid. Transl. Mater. Res. 5, 034001 (2018)
- 30. G. Nagarjuna et al., Impact of redox-active polymer molecular weight on the electrochemical properties and transport across porous separators in nonaqueous solvents. J. Am. Chem. Soc. 136, 16309-16316 (2014).
- 31. K. H. Hendriks et al., High-performance oligomeric catholytes for effective macromolecular separation in nonaqueous redox flow batteries. ACS Cent. Sci. 4, 189-196 (2018).
- 32. Z. T. Gossage et al., Interrogating charge storage on redox active colloids via combined Raman spectroscopy and scanning electrochemical microscopy. Langmuir 33, 9455-9463 (2017).
- 33. S. E. Doris et al., Macromolecular design strategies for preventing active-material crossover in non-aqueous all-organic redox-flow batteries. Angew. Chem. Int. Ed. Engl. 56, 1595-1599 (2017).
- 34. M. Burgess, J. S. Moore, J. Rodríguez-López, Redox active polymers as soluble nanomaterials for energy storage. Acc. Chem. Res. 49, 2649-2657 (2016).
- 35. D. R. Nevers, F. R. Brushett, D. R. Wheeler, Engineering radical polymer electrodes for electrochemical energy storage. J. Power Sources 352, 226-244 (2017).
- 36. K. Hernandez-Burgos, Z. J. Barton, J. Rodriguez-Lopez, Finding harmony between ions and electrons: New tools and concepts for emerging energy storage materials. Chem. Mater. 29, 8918-8931 (2017).
- 37. A. P. Esser-Kahn, S. A. Odom, N. R. Sottos, S. R. White, J. S. Moore, Triggered release from polymer capsules. Macromolecules 44, 5539-5553 (2011).
- 38. C. S. Sevov et al., Physical organic approach to persistent, cyclable, low-potential electrolytes for flow battery applications. J. Am. Chem. Soc. 139, 2924-2927 (2017).
- 39. C. B. Santiago, J. Y. Guo, M. S. Sigman, Predictive and mechanistic multivariate linear regression models for reaction development. Chem. Sci. (Camb.) 9, 2398-2412 (2018).
- 40. S. G. Robinson, Y. Yan, K. H. Hendriks, M. S. Sanford, M. S. Sigman, Developing a predictive solubility model for monomeric and oligomeric cyclopropenium-based flow battery catholytes. J. Am. Chem. Soc. 141, 10171-10176 (2019).

- 41. Y. Yan, S. G. Robinson, M. S. Sigman, M. S. Sanford, Mechanism-based design of a high-potential catholyte enables a 3.2 V all-organic nonaqueous redox flow battery. J. Am. Chem. Soc. 141, 15301-15306 (2019).
- 42. C. Li et al., Polysulfide-blocking microporous polymer membrane tailored for hybrid Li-sulfur flow batteries. Nano Lett. 15, 5724-5729 (2015).
- 43. S. E. Doris, A. L. Ward, P. D. Frischmann, L. J. Li, B. A. Helms, Understanding and controlling the chemical evolution and polysulfide-blocking ability of lithium-sulfur battery membranes cast from polymers of intrinsic microporosity. J. Mater. Chem. A 4, 16946-16952 (2016).
- 44. A. L. Ward et al., Materials genomics screens for adaptive ion transport behavior by redox-switchable microporous polymer membranes in lithium-sulfur batteries. ACS Cent. Sci. 3, 399-406 (2017).
- 45. M. J. Baran et al., Design rules for membranes from polymers of intrinsic microporosity for crossover-free aqueous electrochemical devices. Joule 3, 2968–2985 (2019).
- 46. Anonymous, Sepion Technologies, Advanced membranes for batteries and water (2015). https://www.sepiontechnologies.com/. Accessed 2 April 2020.
- 47. B. A. Helms, D. S. Seferos, Virtual issue: Designing polymers for use in electrochemical energy storage devices. Macromolecules 52, 1349-1353 (2019).
- 48. Z. Li et al., Air-breathing aqueous sulfur flow battery for ultralow-cost long-duration electrical storage. Joule 1, 306-327 (2017).
- 49. Y. M. Chiang, L. Su, M. S. Pan, Z. Li, Lowering the bar on battery cost. Joule 1, 213–219 (2017).
- 50. Anonymous, Form Energy (2019), Energy storage to enable a 100% renewable energy future. https://formenergy.com/, Accessed 3 April 2020.
- 51. J. M. Zheng et al., How to obtain reproducible results for lithium sulfur batteries? J. Electrochem, Soc. 160, A2288-A2292 (2013).
- 52. M. Shin et al., Effect of the hydrofluoroether cosolvent structure in acetonitrile-based solvate electrolytes on the Li⁺ solvation structure and Li-S battery performance. ACS Appl. Mater. Interfaces 9, 39357–39370 (2017).
- 53. A. Andersen et al., Structure and dynamics of polysulfide clusters in a nonaqueous solvent mixture of 1,3-dioxolane and 1,2-dimethoxyethane. Chem. Mater. 31, 2308-2319 (2019).
- 54. Q. Pang et al., Tuning the electrolyte network structure to invoke quasi-solid state sulfur conversion and suppress lithium dendrite formation in Li-S batteries. Nat. Enerav 3, 783-791 (2018).
- 55. C. W. Lee et al., Directing the lithium-sulfur reaction pathway via sparingly solvating electrolytes for high energy density batteries. ACS Cent. Sci. 3, 605-613 (2017).
- 56. H. Wang et al., Tailored reaction route by micropore confinement for Li-S batteries operating under lean electrolyte conditions. Adv. Energy Mater. 8, 1800590 (2018). 57. H. Wang et al., In situ NMR observation of the temporal speciation of lithium sulfur
- batteries during electrochemical cycling. J. Phys. Chem. C 121, 6011-6017 (2017). 58. M. Asadi et al., A lithium-oxygen battery with a long cycle life in an air-like atmo-
- sphere. Nature 555, 502-506 (2018). 59. A. Jain et al., Commentary: The Materials Project: A materials genome approach to
- accelerating materials innovation. APL Mater. 1, 011002 (2013).
- 60. P. Canepa et al., Odyssey of multivalent cathode materials: Open questions and future challenges. Chem. Rev. 117, 4287-4341 (2017).
- 61. T. N. Chen, G. S. Gautam, W. X. Huang, G. Ceder, First-principles study of the voltage profile and mobility of Mg intercalation in a chromium oxide spinel. Chem. Mater. 30, 153-162 (2018)
- 62. L. Hu et al., Tailoring the electrochemical activity of magnesium chromium oxide towards Mg batteries through control of size and crystal structure. Nanoscale 11, 639-646 (2019).
- 63. B. J. Kwon et al., Probing electrochemical Mg-ion activity in MgCr2-xVxO4 spinel oxides. Chem. Mater. 32, 1162-1171 (2020).
- 64. N. Sa et al., Direct observation of MgO formation at cathode electrolyte interface of a spinel MgCo2O4 cathode upon electrochemical Mg removal and insertion. J. Power Sources 424, 68-75 (2019).
- 65. H. D. Yoo et al., Intercalation of magnesium into a layered vanadium oxide with high capacity. ACS Energy Lett. 4, 1528-1534 (2019).
- 66. X. Q. Sun et al., A high capacity thiospinel cathode for Mg batteries. Energy Environ. Sci. 9, 2273-2277 (2016).
- 67. P. Bonnick et al., Insights into Mg2+ intercalation in a zero-strain material: Thiospinel MgxZr2S4. Chem. Mater. 30, 4683-4693 (2018).
- 68. C. Kim et al., Multivalent electrochemistry of spinel MgxMn3-xO4 nanocrystals. Chem. Mater. 30, 1496-1504 (2018).
- 69. J. L. Andrews et al., Reversible Mg-ion insertion in a metastable one-dimensional polymorph of V2O5. Chem 4, 564-585 (2018).
- 70. S. D. Han et al., Mechanism of Zn insertion into nanostructured delta-MnO2: A nonaqueous rechargeable Zn metal battery. Chem. Mater. 29, 4874–4884 (2017).
- 71. A. L. Lipson et al., Rechargeable Ca-ion batteries: A new energy storage system. Chem. Mater. 27, 8442-8447 (2015).
- 72. K. Ta et al., Understanding Ca electrodeposition and speciation processes in nonaqueous electrolytes for next-generation Ca-ion batteries. ACS Appl. Mater. Interfaces 11, 21536-21542 (2019).
- 73. K. S. Nagy, S. Kazemiabnavi, K. Thornton, D. J. Siegel, Thermodynamic overpotentials and nucleation rates for electrodeposition on metal anodes. ACS Appl. Mater. Interfaces 11, 7954-7964 (2019).
- 74. A. Shyamsunder, L. E. Blanc, A. Assoud, L. F. Nazar, Reversible calcium plating and stripping at room temperature using a borate salt. ACS Energy Lett. 4, 2271-2276 (2019).
- 75. N. N. Rajput, X. Qu, N. Sa, A. K. Burrell, K. A. Persson, The coupling between stability and ion pair formation in magnesium electrolytes from first-principles quantum mechanics and classical molecular dynamics. J. Am. Chem. Soc. 137, 3411-3420 (2015).

2020

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- K. C. Lau et al., Widening electrochemical window of Mg salt by weakly coordinating perfluoroalkoxyaluminate anion for Mg battery electrolyte. J. Electrochem. Soc. 166, A1510–A1519 (2019).
- Z. Q. Rong et al., Materials design rules for multivalent ion mobility in intercalation structures. Chem. Mater. 27, 6016–6021 (2015).
- Z. Rong et al., Fast Mg2+ diffusion in Mo-3(PO4) O-3 for Mg batteries. Chem. Commun. (Camb.) 53, 7998–8001 (2017).
- D. C. Hannah, G. Sai Gautam, P. Canepa, Z. Rong, G. Ceder, Magnesium ion mobility in post-spinels accessible at ambient pressure. *Chem. Commun. (Camb.)* 53, 5171–5174 (2017).
- P. Canepa et al., High magnesium mobility in ternary spinel chalcogenides. Nat. Commun. 8, 1759 (2017).
- N. E. R. Zimmermann *et al.*, Electrostatic estimation of intercalant jump-diffusion barriers using finite-size ion models. J. Phys. Chem. Lett. 9, 628–634 (2018).
- N. N. Rajput, T. J. Seguin, B. M. Wood, X. Qu, K. A. Persson, Elucidating solvation structures for rational design of multivalent electrolytes—A review. *Top. Curr. Chem.* 376, 19 (2018).
- S. H. Lapidus et al., Solvation structure and energetics of electrolytes for multivalent energy storage. Phys. Chem. Chem. Phys. 16, 21941–21945 (2014).
- T. J. Seguin, N. T. Hahn, K. R. Zavadil, K. A. Persson, Elucidating non-aqueous solvent stability and associated decomposition mechanisms for Mg energy storage applications from first-principles. *Front Chem.* 7, 175 (2019).
- P. Canepa et al., Understanding the initial stages of reversible Mg deposition and stripping in inorganic nonaqueous electrolytes. Chem. Mater. 27, 3317–3325 (2015).
- P. Canepa et al., Elucidating the structure of the magnesium aluminum chloride complex electrolyte for magnesium-ion batteries. Energy Environ. Sci. 8, 3718–3730 (2015).
- N. T. Hahn et al., Enhanced stability of the carba- closo-dodecaborate anion for highvoltage battery electrolytes through rational design. J. Am. Chem. Soc. 140, 11076– 11084 (2018).

- C. Wadia, P. Albertus, V. Srinivasan, Resource constraints on the battery energy storage potential for grid and transportation applications. J. Power Sources 196, 1593–1598 (2011).
- E. A. Olivetti, G. Ceder, G. G. Gaustad, X. K. Fu, Lithium-ion battery supply chain considerations: Analysis of potential bottlenecks in critical metals. *Joule* 1, 229–243 (2017).
- B. Ballinger et al., The vulnerability of electric vehicle deployment to critical mineral supply. Appl. Energ. 255, 113844 (2019).
- 91. J. Janek, W. G. Zeier, A solid future for battery development. *Nat. Energy* 1, 16141 (2016).
- X. Y. Zheng et al., Sodium metal anodes for room-temperature sodium-ion batteries: Applications, challenges and solutions. Energy Storage Mater. 16, 6–23 (2019).
- P. K. Nayak, L. Yang, W. Brehm, P. Adelhelm, From lithium-ion to sodium-ion batteries: Advantages, challenges, and surprises. *Angew. Chem. Int. Ed. Engl.* 57, 102–120 (2018).
- Y. S. Tian et al., Reactivity-guided interface design in Na metal solid-state batteries. Joule 3, 1037–1050 (2019).
- J. G. Connell et al., Crystal orientation-dependent reactivity of oxide surfaces in contact with lithium metal. ACS Appl. Mater. Interfaces 10, 17471–17479 (2018).
- Y. S. Zhu et al., Dopant-dependent stability of garnet solid electrolyte interfaces with lithium metal. Adv. Energy Mater. 9, 1803440 (2019).
- I. Villaluenga et al., Compliant glass-polymer hybrid single ion-conducting electrolytes for lithium batteries. Proc. Natl. Acad. Sci. U.S.A. 113, 52–57 (2016).
- D. Buttrey et al., Electrical Energy Storage Factual Status Document. https://science. osti.gov/-/media/bes/pdf/reports/2017/EES_BRN_Factual_Doc.pdf?la=en&hash= 07F45BB24AD0C27CBD545A948AAB24D851B61FAE. Accessed 12 May 2020.
- G. Crabtree, E. Takeuchi, G. Rubloff, Basic Research Needs for Next Generation Electrical Energy Storage. https://science.osti.gov/-/media/bes/pdf/brochures/2017/ BRN-NGEES_rpt-low-res.pdf?la=en&hash=0DEB8D525053595FEEEB75BB52F02D19E43F149F. Accessed 12 May 2020.