Advances in Electrochemical Science and Engineering

Alkire, Bartlett, Koper (Eds.)

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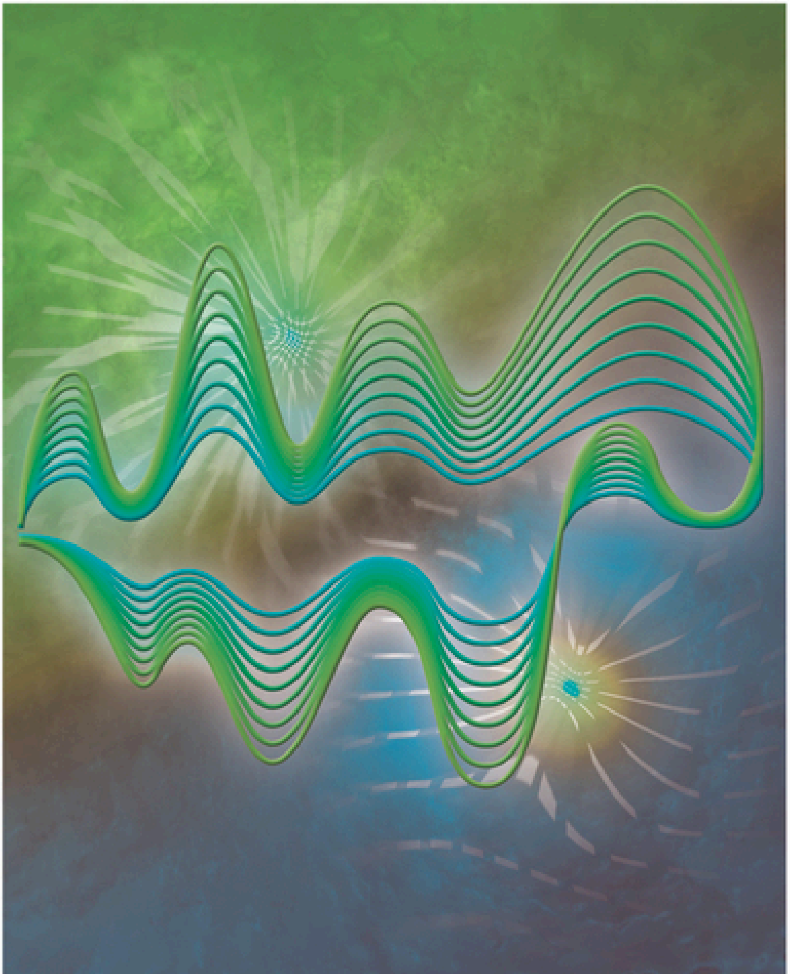
Electrochemical Engineering

From Discovery to Product



Volume 18

Edited by
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and Marc T. Koper

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In collaboration with the International Society of Electrochemistry

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Electrochemical Engineering: The Path from Discovery to Product

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Series Preface

It is with sincere gratitude that we express appreciation to our co-editor and good friend, Professor Jacek Lipkowski, who has indicated his desire to bring more than two decades of editorial leadership to closure with his 2017 publication of Volume 17 of this series, entitled "Nanopatterned and Nanoparticle-Modified Electrodes." His deep technical knowledge and gracious personal manner have made it a genuine pleasure to work with him through the years.

With this volume, we are pleased to welcome Professor Marc Koper as co-editor. Professor Koper studied chemistry at the University of Utrecht (the Netherlands) and the Université Libre de Bruxelles and received his PhD from the University of Utrecht in 1994. After a postdoctoral stay at the University of Ulm (Germany), he first became research fellow and then Associate Professor at the Eindhoven University of Technology. In 2005, he moved to Leiden University (the Netherlands) where he is currently a professor of fundamental surface science. His research interests focus on electrocatalysis, electrochemical surface science, and theoretical and computational electrochemistry. Marc Koper is a member of the Royal Netherlands Academy of Arts and Sciences, fellow of the International Society of Electrochemistry, and has received awards from the Royal Society of Chemistry, the International Society of Electrochemistry, and The Electrochemical Society.

The purpose of this series is to provide high-quality advanced reviews of topics of both fundamental and practical importance for the experienced reader.

Preface

The path from scientific discovery to impact on society has many steps. Today, new science and engineering approaches are being developed to facilitate that task of moving atomistic-scale discoveries and understanding into well-engineered products and processes based on electrochemical phenomena. However, people working on one particular application often find it difficult to recognize highly relevant new methods that were developed for entirely different applications. That is, especially at the atomistic scale, routine science and engineering methodologies are still in an early phase of development for use in assessing emerging business opportunities.

Therefore, the focus for each chapter in this volume includes not only the overarching science and engineering roadblocks that were faced, but also the *reusable* approaches that were developed to inform the technological/business applications with the underlying atomistic science. Many such reusable methods could be relevant beyond their initial use. Bringing together such approaches for diverse applications that span the nano–bio–photo–micro landscape will facilitate recognition and cross-fertilization between seemingly different applications and will lessen the need to "reinvent the wheel" for each.

Alivisatos and Osowiecki, in their Introductory Perspective, emphasize the central importance of the value to society of new candidate technologies. Whether a proposed breakthrough is valuable enough depends in large part on its theoretical performance limits as compared to the current state of the art. Also important for electrochemical applications are selectivity and control of the desired reaction. They illustrate these points with the example of quantum dots, once unusual materials that are today produced at the ton scale and used in commercial display technologies. They comment on several electrochemical applications where considerations based on limits-selectivity-control could provide guideposts on the path from discovery to product.

Brushett describes a new paradigm for battery research: tight integration of discovery science, battery design, research prototyping, and manufacturing collaboration within a single highly interactive organization. This new paradigm, pursued at the Joint Center for Energy Storage Research (JCESR), seeks transformational change in transportation and the electric grid driven by next-generation, high-performance, low-cost electrochemical energy storage. Although JCESR focuses exclusively on "beyond lithium-ion batteries," the overall systems approach is portable and can be applied to other applications in order to accelerate the pace of discovery and innovation, while reducing the time from conceptualization to commercialization. To this end, the chapter presents JCESR's motivation, vision, mission, as well as outcomes and lessons learned in the development, execution, and refinement of this mode of operation.

Balsara and colleagues review the redox pathways that have been proposed for the cathode of a Li–S cell as it is charged and discharged. The use of various *in situ* spectral methods to identify the fingerprints of reaction intermediates is discussed. The electrode design required of such methods should guarantee unimpeded access to the species of interest and avoid transport bottlenecks. The basis for understanding the role of the electrolyte for achieving high specific energy is described. The general approach, based on in situ spectroelectrochemical methods, is reusable for other electrochemical systems where intermediate steps in the overall reaction are not yet resolved, such as in alkaline fuel cells and carbonate- or ether-based electrolytes.

Deligianni and coworkers describe the scientific and technological path from laboratory research to early industrial development of electrodeposition for inorganic solar cells. An overarching consideration is to design earth-abundant materials whose elements are amenable to massive-scale application. The chapter describes initial investigations on copper–indium–gallium–diselenide (CIGS) solar cells, before turning to fabrication approaches used for electrodeposited precursor materials, associated fundamentals of electrodeposition, and development of solution chemistries for copper-based earth-abundant electrodeposited kesterite precursor materials such as Cu_2ZnSn (Se,S). A comprehensive description of scale-up procedures is described from the laboratory scale of a rotating disk, to 15 × 15 cm glass plates, to 30 × 60 cm modules, and full-size 60–120 cm module, leading up to an industrial-scale production line for producing solar cells at the rate of $1\ m^2\ min^{-1}$.

Ohashi describes the perspectives in Japan that guided evolution of the thin film head technology within the hard disk drive business sector. The technical issues included understanding the properties of candidate magnetic materials and their suitability for use in thin film heads, such as stress, thermal decay, and noise emanating from domain walls of finite thickness. The business issues included recognizing trade-offs between different candidate technologies whose suitability depended on the application. The fluid state of new technologies and new business opportunities creates "The Innovator's Dilemma," which occurs when a new technology brings a value proposition that is different from any ever proposed by existing customers, that is, choosing between sustaining a proven path forward and investing in a potentially disruptive technology.

Orazem and colleagues address the problem of separating water from clay suspensions generated as a waste stream in beneficiation of phosphate ores. The sequential development of a continuous electrokinetic separation process was accomplished with experimental and computational methods that moved atomistic-scale discoveries and understanding toward a well-engineered process. The approach involved empiricism guided by understanding how solids content depended on applied electric field and elapsed time. While electron microscopy and surface analyses provided insight into the structure of the clay, the design of successive prototypes relied on intuition, insights gained from previous prototypes and informed engineering judgment.

Taylor and coworkers investigate pulse reverse-current electroplating and surface-finishing operations. While there are well-establish traditional paradigms for such processes, the authors report various research and development activities carried out with a balance between current fundamental understandings combined with a willingness to pursue non-conforming observations that lead them to paradigm-breaking conclusions. Examples include copper electrodeposition with pulse-reverse cathodic current and decreased used of chemical additives, deburring of non-passive metals with use of forward-only anodic pulses, deburring of passive metals with reverse-pulse anodic and decreased hydrogen evolution, and pulse reverse voltage electropolishing of niobium that uses low concentration acid devoid of HF.

Tsukuhara describes development of a trace moisture sensor that was developed via a series of investigations, spanning several decades, of puzzling phenomena and blind alleys in their pursuit. The tortuous path from discovery to product included non-intuitive results, failed hypotheses, unexpected phenomena, and the need to rethink past observations. All of these roadblocks served to seed fresh ideas guided by background knowledge of laser ultrasonics, surface acoustic waves, propagation of waves in elastic spheres, hydrogen interaction with Pd/Ni films, deposition of amorphous silica, and chemical interaction of water with silica glass, among others. The guiding strategies that emerged from this project include the following: find the thermodynamic limit, do not dismiss something that is apparently wrong, think about observations many times over and be prepared to change you previous opinions, test experiments with numerical simulation, and look broadly into cumulative knowledge available in other fields.

Williams reports on development of low-cost sensors based on gas-sensitive semiconducting oxides. A key concept illustrated in this case is to focus on what limits the path forward. For example, the central technical requirement involved correct control of the sensor and sample, while the economic barriers included the cost of calibration, maintenance, and the cost of an erroneous or unreliable reading. These constraints, along with the knowledge of fundamental science aspects of high sensitivity and low selectivity, led to innovative design of catalyst layers and T-programmed desorption routines. The scientific and engineering threads brought together in this work included understanding surface reactions on semiconducting oxide, sensor development, instrument development, and big data associated with the application. These illustrate how deep scientific understanding led to well-engineered products and markets for them, which, in turn, generated questions that further stimulated the quest for knowledge in fields that were never in view at the start.

In the long run, the reduction to routine use of such methods as described in this volume will provide the foundation for next-generation science and engineering at the molecular scale. In this spirit, we take inspiration from Carl Wagner,[1] who wrote in an earlier volume of this series:

> … molecular engineering may be important in the future development of industrial electrochemical processes.

June, 2018

Richard Alkire
Urbana

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1

Introductory Perspectives

A. Paul Alivisatos [1,2,3,4] *and Wojciech T. Osowiecki* [1,2]

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The path from a scientific discovery to a commercial product is a long one, with many twists and turns. It is easy to list many examples of potential breakthroughs that never crystallized into real-life solutions. Instead, this book takes the approach of finding the best examples of discoveries that either have already been able to deliver products or are on their way to accomplish this goal. Each chapter discusses a different field, as we believe that there exist certain themes that unite all these success stories.

In order to create a viable product, one has to be brutally honest about what is actually likely to be of genuine value to society, represented by real markets. Many projects and companies struggle if they cannot realize what is fundamentally distinctive about their technology and whether the proposed breakthrough is valuable enough. This conceptualization of what makes a technology distinctive almost necessarily has to be in reference to its theoretical performance limits as compared to the current state of the art.

This comparison between limits and current performance informs the researcher of not only how long the path forward is, but also whether the new technology has any chance of supplanting others or of creating a new market. Research is very complex and unpredictable, and often, we see a clear progression of discoveries that "tell a story" only after the fact. Nevertheless, the question regarding maximum theoretical limits should never leave our minds. Only then can we focus on putting our efforts into the most promising endeavors.

In the case of electrochemical transformations, the most important issues to address after the theoretical limits are selectivity and control of the desired reaction. For example, how do we make sure that the bonds that break and form are ones that we intended and that the desired products are obtained? Sometimes, the inspiration can come from nature and other scientific fields. Enzymes control reactions with an awe-inspiring degree of precision, forming exactly the compounds organisms need, and reminding us how sophisticated and optimized chemical environments can be. Although scientists did not have billions of years

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of evolution to perfect their processes, this book is also intended as a reminder to look beyond one's area of expertise for encouragement and fresh ideas.

So how can the ideas of theoretical limits and control be applied in electrochemical engineering? The challenges of the current world dictate opportunities for researchers, especially those interested in seeing their work incorporated in crucial technological innovations of the future. In the twenty-first century, supplying energy to the ever-growing global population in a sustainable manner is, without doubt, one of the most important such challenges.

Each year, the U.S. Energy Information Administration forecasts changes in energy generation for the next few decades and we expect to see significant shifts in the fuel mix; as market forces oblige coal plants to retire, they will be successively replaced by renewable sources and oil and gas (Figure 1.1). Among the renewable sources, solar and wind energy are particularly enticing to the electrochemical community, as they promise a growing supply of cheaper electrons, decoupled from environmentally costly fossil fuel combustion.

In this new economy, scientists should be encouraged to think of electrons as crucial and readily available chemical reagents. Just like fossil fuel industry turned oil into a ubiquitous precursor to many compounds and products, now electrons will be involved in crucial processes such as fuel generation and energy storage. Indeed, the ability to store energy in chemical bonds solves one of the greatest challenges for renewables, namely their transience. Energy storage brings opportunities for a distinctive set of technologies to emerge.

We believe that in order to use electrons properly, the issues, highlighted above, of (i) *theoretical efficiency limits* and (ii) *control* must be addressed. To start,

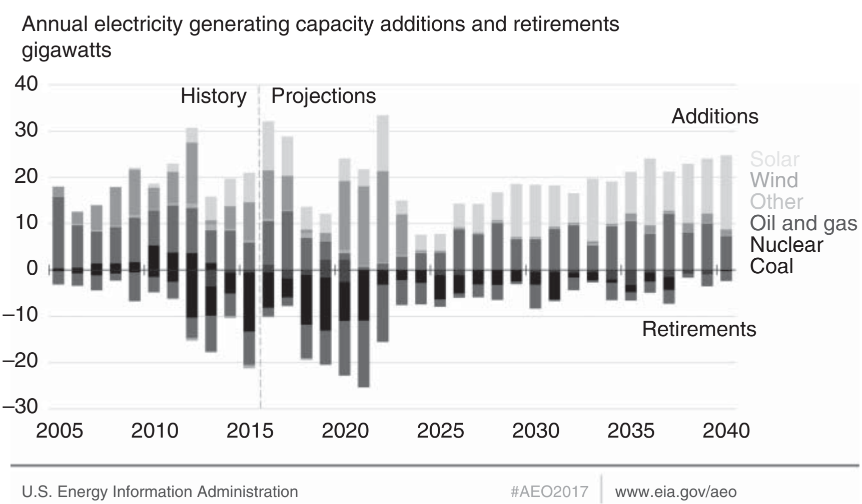

Figure 1.1 Annual electricity-generating capacity additions and retirements. Most of the wind capacity is expected to be built before the scheduled expiration of the production tax credit in 2023, although wind is likely to remain competitive without the credits. Substantial cost reductions and performance improvements strongly support continuous solar generation growth.

let us consider a field that the authors of this foreword are particularly familiar with: quantum dots (QDs). QDs are small semiconducting nanoparticles that possess bound, discrete electronic states [1]. The optoelectronic properties of these dots depend on the size and shape: the larger the particles are, the longer the wavelength of the emitted light is. After a long period of discovery and development, these once unusual materials are produced today at the ton scale and used in commercial display technologies. Their most distinctive edge comes from the color purity of their emission, which creates displays that realize a broader color gamut than previous technologies did.

For current commercial quantum dot display devices, such as televisions, the efficiency of light emission following absorption of a higher energy blue pump photon is crucial for the success of the product. Energy from every absorbed blue photon must be emitted as a green or red photon to form the full color image. The desired radiative rate competes with non-radiative processes that emit phonons instead of photons. Phonon emission not only decreases energy efficiency but also causes unwanted heating that may lead to device failure. This competition is measured by the quantum yield (QY): rate of radiative emissions divided by all rates. An ideal situation, where all energy is released as light, corresponds to the QY of 100%, also known as the unity QY.

As there is no *fundamental limitation* on particles achieving the unity QY (or at least 99.999%), scientists have been working for decades on perfecting synthetic recipes and treatments to get to this limit. Although initial QYs reported for CdS were below 1%, [2] it was very important to conceive of the then-unachievable maximum potential of QDs with much higher yields for biological and optical applications. The *selectivity and control* came with increased understanding of surface-related trap states, arising from insights spanning the fields of semiconductor surface chemistry, optics, electron microscopy, and theoretical modeling. A large community worked together in "constructive competition" to achieve relevant breakthroughs. Thanks to techniques such as particle shelling, [3] QYs were brought significantly above 90% [4]. With QD displays now successfully penetrating the market of TVs and electronic displays, scientists are already exploring new materials, such as perovskites [5, 6], to bring us even closer to the unity QY.

We believe that the same themes of finding maximum efficiency limits and reaching toward them by increasing control and understanding of the researched process apply to the fields presented in this book. Solar cell efficiencies are always compared to the famous Shockley–Queisser (SQ) limit. Although it concerns only a single p–n junction, the number of 33% has motivated researchers and engineers to search for continuous improvements [7]. Today, the market opportunity for a new single band gap technology is narrow because even if it exceeds the current 20% power efficiency of silicon and thin film technologies, it will likely at best be niche, while the ceiling of 33% is not that far off from the current technologies. Scientists may well be advised to look at technologies that naturally lend themselves to multi-gap configurations that have the potential to exceed the SQ limit. Likewise, by performing thermodynamic analysis, one can understand why scientists are excited about Li/air and Li/O_2 batteries. The latter can theoretically achieve 10 times higher energy density than present Li-ion batteries [8].

Currently, long-term stability issues are plaguing these devices but the promise set by the thermodynamic limit is worth years of research pursuing better control of charge/discharge cycles [9].

Another electrochemical field worth mentioning is catalysis, especially CO_2 reduction. From the perspective of thermodynamics, conversion of carbon dioxide to fuels such as ethanol should not be very energetically costly [10]. In reality, a large overpotential is needed to obtain an appreciable amount of reaction products [11]. Additionally, things get complicated due to lack of selectivity. Catalysis with Cu generates up to 16 different chemical species [10]. In electrochemistry, one can always adjust the voltage to speed up the reaction as long as it is kinetically controlled, but with poor control over the catalyst, there are too many electrons going into wrong places. We see here an analogy to exciting a semiconducting quantum dot significantly above the bandgap. High energy excitation increases the absorption of quantum dots and increases the rate of the electrochemical transformation. In both cases, however, the extra energy above a threshold opens up many new unwanted pathways, and in the quest for higher rates, it is easy to end up with unwanted processes. Is it possible to properly engineer the system to avoid them? Scientists are currently working on extending control over this reaction, and we hope to learn more about how to selectively form desired products.

We wish we could finish this foreword with a list of specific steps that scientists can take to guarantee improvement in the selectivity and control of solar cells, batteries, and catalysts. Instead, we have highlighted what we consider to be some of the important steps to consider while researching into improving these technologies. While the theoretical efficiency limits may never be achieved, the thermodynamic analyses will illuminate the most promising uses of electrons; the great challenge for the new generation of electrochemists is to conceive of entirely new approaches to guide reactions at the electrochemical interface by means that have not yet been tried. Creative nano-engineering seems as if it might be the key. Explicit thinking about the role of fluctuations and the creation of more structured sequences of local environments seem like they may lead to breakthroughs. We hope that this book will inspire scientists to consider their own research plans with equal measure of thought given to the limit of what may be possible and to the actuality of what is achieved in practice today. The path from discovery to product will surely prove fruitful if followed with both a realistic and ambitious mind.

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2

The Joint Center for Energy Storage Research: A New Paradigm of Research, Development, and Demonstration

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Established in 2012, the Joint Center for Energy Storage Research (JCESR) is an Energy Innovation Hub managed by the United States Department of Energy's Office of Basic Science with a mission of developing the next generation of high-performance, low-cost electrochemical energy storage technologies for transportation and the electric grid. In pursuit of this transformative vision, JCESR introduced a new paradigm for battery research, integrating discovery science, battery design, and prototyping in a single, interactive organization, to accelerate discovery and innovation, to reduce the time from conceptualization to commercialization, and ultimately, to bridge the dreaded "valley of death" between research and industry. While JCSER exclusively focuses on energy storage, this organizational paradigm is malleable and can be applied to numerous technological challenges of societal importance. Thus, while JCESR's scientific accomplishments are described in the peer-reviewed literature, there is considerable value in disseminating JCESR's strategic approaches to promoting breakthrough energy science. This chapter seeks to provide insight into JCESR's mission and organizational structure, as well as to highlight important tools used to effectively connect research activities across the spectrum, from fundamental discovery science to cell design and prototyping intended to enable commercial deployment.

2.1 Background and Motivation

A grand challenge of the twenty-first century will be the evolution of the electrical power system (grid) to meet emerging energy demands while balancing environmental stewardship and cost-effectiveness. In the United States, 82% of the total energy consumed is derived from fossil fuel sources (i.e. oil, coal, and natural gas), dominated by use for electricity and transportation [1]. However, in

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the future, this dependence will not be feasible [2], as rising population and continuing economic growth in the developing world are projected to double global energy consumption by 2050 [3]. Moreover, the continued and increasing generation of anthropogenic carbon dioxide (CO_2) from fossil fuel combustion will likely have negative implications for the global climate [4]. Thus, a tremendous need exists for scientific and technological advances to address these challenges, sparking worldwide investment in low carbon/carbon neutral power generation, carbon capture and storage, and system-wide energy efficiency [5, 6].

Decarbonization of electricity generation will require the widespread integration of renewable, non-dispatchable energy sources (e.g. solar photovoltaic (PV), wind). However, the uncontrollable intermittency of these generation sources often leads to mismatches in electricity supply and demand, and thus only 15% of the US grid electricity is produced by renewables [7]. Energy storage technologies can smooth and meter the delivery of electricity from these variable resources as well as offset congestion issues within transmission and distribution infrastructure, thus deferring costly investments. Increased energy storage assets can also provide a range of high value services including grid stabilization and resiliency through backup power, introducing new revenue streams for a range of stakeholders [8].

2.2 Lithium-ion Batteries: Current State of the Art

Electrochemical energy storage, specifically rechargeable batteries, is poised to enable widespread penetration of electric vehicles to replace fossil fuels with electricity, reduce carbon emissions, and improve efficiency. Moreover, batteries can advance the grid by replacing its just-in-time delivery system with local inventories of stored energy that can be built up or drawn down to buffer time gaps in variable supply (i.e. intermittent renewable sources) and variable demand (i.e. customer needs). Both of these sectors require energy storage solutions with performance and cost metrics beyond the trajectory of current leading technology, spurring the formation of JCESR as an Energy Innovation Hub with a bold vision of creating next-generation battery technologies with the potential to transform the transportation sector and the electric grid in the same way lithium-ion (Li-ion) batteries revolutionized personal electronics.

Li-ion batteries represent the current state-of-the-art in energy storage, ubiquitous in personal electronics, and emergent in transportation and stationary applications. Conceptualized in the early 1970s, and commercialized in the early 1990s [9], Li-ion batteries store and release energy by shuttling lithium cations through an organic electrolyte, accompanied by electrons through an external circuit, between a positive electrode, typically a lithiated transition metal oxide or phosphate, and a negative electrode, typically graphite [10]. Over the past 25 years, Li-ion has become the predominant technology, due to its high energy density, good cycle life, and high charge/discharge efficiency, and has rapidly developed driven by scale, materials advancements, and manufacturing improvements. Indeed, over the past decade, Li-ion batteries have improved their energy density by 5% per year and reduced their cost by 8% per year [11]. A vibrant research topic, with ongoing contributions from academe, national laboratory, and industrial researchers, continued incremental improvements in energy density, lifetime, and cost can be expected for the foreseeable future. Yet, successive improvements in the technology are not anticipated to yield the affordable, high energy density storage required for transformational change in transportation or the grid.

2.3 Beyond Li-Ion Batteries

In contrast, the beyond Li-ion battery space is much larger, richer, and far less explored than the current Li-ion battery space. Unlike the single concept of intercalation at a negative and positive electrode in commercial Li-ion batteries, beyond Li-ion batteries embrace a wealth of novel concepts, including multiply charged working ions in place of singly charged lithium, high energy covalent chemical reactions at the electrodes in place of intercalation, and fluidized active materials in place of crystalline electrodes. These three energy storage concepts: multivalent intercalation, chemical transformation, and nonaqueous flow, detailed later, are the primary research directions that JCESR pursues. They are fundamentally different from the intercalation concept of commercial Li-ion batteries, have the potential of enabling transformative performance enhancements and cost reductions, as well as providing significantly greater design and operational flexibility and opportunity than commercial Li-ion batteries.

Despite this broad design space, at JCESR's inception, few researchers were exploring these opportunities as compared to conventional Li-ion battery research. Indeed, with a clear market and established value chains, incremental improvements in performance and cost of Li-ion batteries can produce high returns. There is significant risk in attempting to create an entirely new technology as this requires the discovery, development, and application of at least three new materials (one each for the negative electrode, electrolyte/membrane, and positive electrode), which must work harmoniously for the device to function. This represents a daunting challenge, beyond the resources of most research groups and small-to-medium sized companies, and thus necessitates a new approach to battery research. To this end, JCESR has assembled a broad multi-institutional team with expertise and resources to explore the possibilities of the beyond Li-ion battery space, to reduce scientific and technological risk encouraging other stakeholders to enter the field, and ultimately to create next-generation battery systems.

2.4 JCESR Legacies and a New Paradigm for Research

In order to accelerate research beyond Li-ion, JCESR developed a new paradigm for research combining discovery science, battery design, and rapid prototyping into a single organization and quantifying its successes through three legacies. Practically, JCESR focuses on novel electrochemical energy storage mechanisms and new device architectures. Researchers across JCESR seek to understand and control the underlying materials and phenomena that govern charge storage and then harness this knowledge to reliably engineer electrochemical cells and systems. To measure the success of JCESR, the organization set forth three quantifiable legacies:

1. *A library of fundamental science of the materials and phenomena of energy storage at atomic and molecular levels.* This library will be freely available through the literature and open source software with the goal of informing, inspiring, and accelerating the work of the broader battery community as "a rising tide lifts all boats." Traditionally, battery research operates by trial and error such that if a new material is developed and shows improved performance, it is adopted and published, while if the new material fails, it is discarded and often not reported. Thus, JCESR will also report candidates examined for improved energy storage, which failed techno-economic (TE) metrics to inform future researchers throughout the community.
2. *Two research prototype batteries one for transportation and one for the grid that, when scaled for manufacturing, achieved five times the energy density and one fifth the cost of current battery technologies at JCESR's inception (2012).* These two prototypes will differ in their format, materials chemistry, and operating conditions, but will be based on the same body of fundamental knowledge generated from the first legacy. Detailed performance metrics are noted below in Table 2.1. Although five years is a short time to achieve this legacy, JCESR has deliberately chosen not to diminish its vision or replace its mission with less aggressive outcomes that carry lower risk but are not transformative.
3. *A new paradigm for battery research and development that integrates discovery science, battery design, research prototyping, and manufacturing collaboration in a single highly interactive organization.* In the traditional battery community, each of these four functions is typically carried out by a separate research team, often in a different location by experts with differing skills, motivations,

Table 2.1 Goal performance metrics for JCESR prototypes when projected to battery packs, as written in the JCESR proposal.

Transportation	Grid
100 \$/kWh	100 \$/kWh
400 Wh kg^{-1} and 400 Wh l^{-1}	95% round-trip efficiency at C/5
800 W kg^{-1} and 800 W l^{-1}	
1000 cycles 80% DoD C/5	7000 cycles at C/5
15-year calendar life	20-year calendar life
EUCAR 2	Safety equivalent to natural gas turbine
Metrics based on a 350-mile range EV	Metrics based on 5 hours of storage

and focus. In JCESR, these four functions are pursued simultaneously and in close cooperation to exploit the dynamic interaction and inspiration that each function draws from the others. For example, early stage research prototyping can reveal battery design issues and discovery science challenges that can be passed rapidly to the appropriate functional team for analysis and solution, thus enriching the scope and expediting the progress of all areas. Such interactions are expected to quicken the pace of discovery and innovation and reduce the time from conceptualization to commercialization.

JCESR's new paradigm for accelerating the development of these energy storage technologies combines discovery science, battery design, research prototyping, and manufacturing consulting in a single, highly interactive, operationally nimble organization (Figure 2.1). Traditionally, in the battery community, fundamental materials discovery and cell engineering occurred separately with slow and periodic communication between them. Figure 2.1 shows the end-to-end innovation pipeline, from fundamental discovery science to manufacturing collaboration, integrated under "one roof" within the JCESR organization. The left portion of the diagram depicts the three transformative storage concepts that JCESR is pursuing, namely, multivalent intercalation, chemical transformation, and nonaqueous redox flow. The multivalent intercalation and chemical transformation concepts focus on transportation applications whereas nonaqueous redox flow focuses on energy-intensive grid applications. JCESR is pursuing these three beyond Li-ion scientific thrusts (Figure 2.2) because they have the theoretical potential to meet the legacy goals. Their active species and cell architecture deviate substantially from conventional Li-ion requiring the breadth of knowledge and expertise researchers at JCESR possess.

Multivalent intercalation utilizes a divalent cation (e.g., Mg^{2+}) instead of a monovalent cation (Li^+), as the intercalant at the battery positive electrode in an attempt to double the charge storage capacity and overall energy as compared to Li-ion [12, 13]. In addition, common multivalent intercalation cations deposit more uniformly than metallic Li during electrochemical cycling, opening the possibility of a metallic negative electrode to further increase the energy density of the system [14, 15]. However, discovering a stable electrode–electrolyte system that supports the plating/stripping at the negative electrode and intercalation at a high-voltage positive electrode remains elusive [16–20].

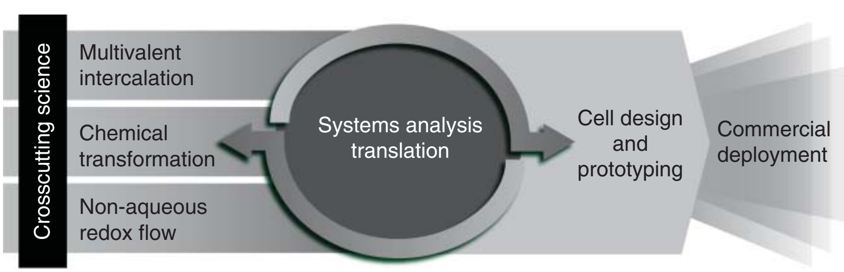

Figure 2.1 JCESR's new paradigm for battery research and development.

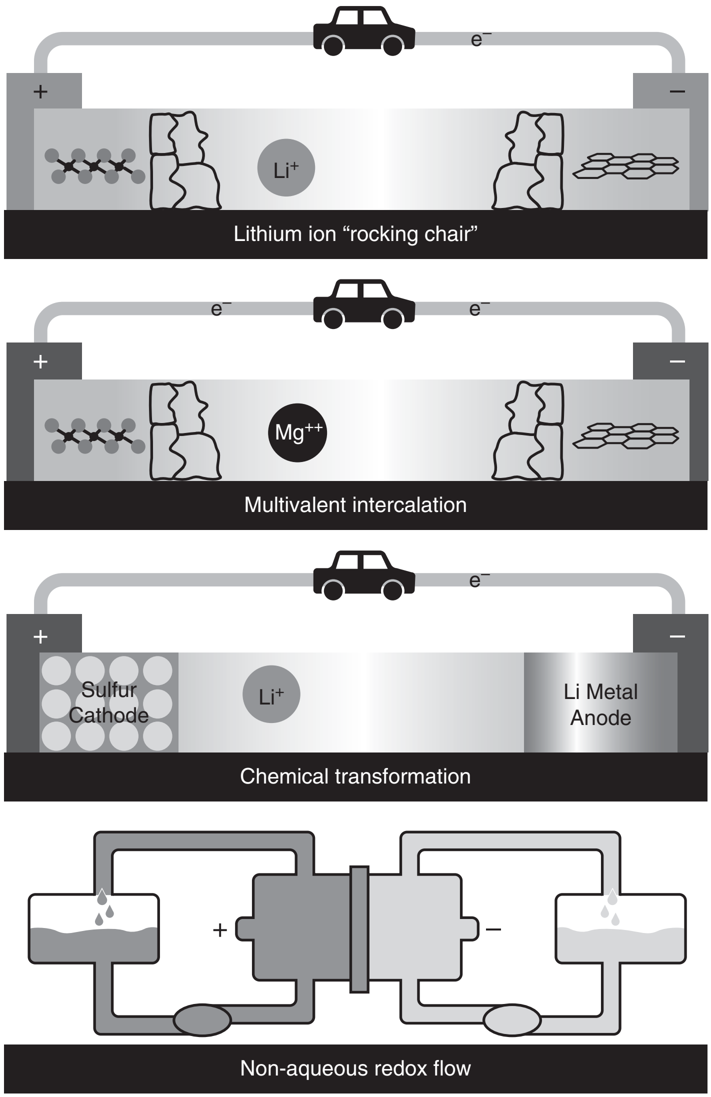

Figure 2.2 JCESR is pursuing three scientific thrusts beyond lithium-ion: multivalent intercalation, chemical transformation, and nonaqueous redox flow.

Chemical transformation harnesses a negative electrode and a positive electrode that rely on a phase change or alloying for storage such as the complete stripping of the metal-negative electrode solid (e.g. Li and Mg) into ions or the conversion between different solid structures through a liquid intermediate at the positive electrode (e.g. sulfur and oxygen). The benefits of these transformations are that more energy per reaction can be accessed and that the materials are inexpensive. However, the side reactions and significant volumetric expansion present in these systems contribute to rapid capacity loss and poor lifetimes [21–26]. Moreover, the knowledge of fundamental reaction mechanisms for these