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Introductory Perspectives

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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,

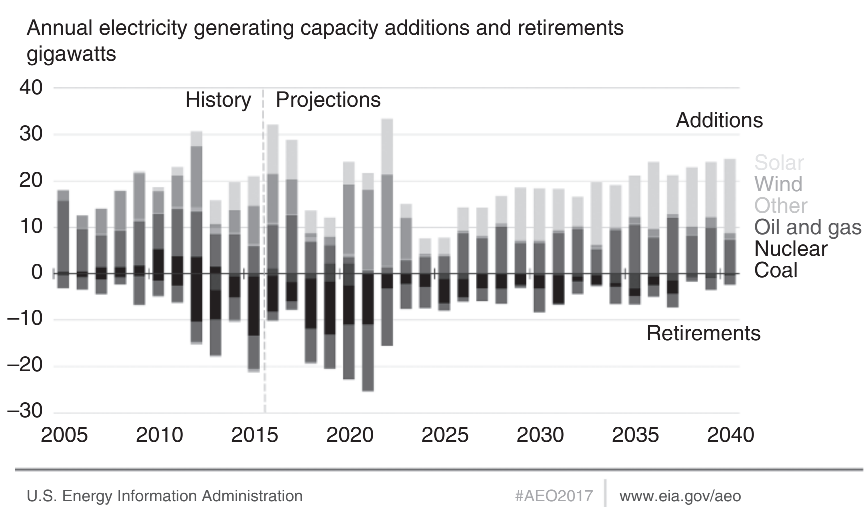

Figure 1.1 Annual electricity-generating capacity additions and retirements. Most of the wind capacity is expected to be built before the scheduled expiration of the production tax credit in 2023, although wind is likely to remain competitive without the credits. Substantial cost reductions and performance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