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The Role of Electrochemical Engineering in Our Energy Future

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Richard Smalley, Nobel Prize-winning chemist (1996) and co-discoverer of buckminsterfullerene (C60), presented a seminar at Columbia University in New York on 23 September 2003. The title of his talk was “Our Energy Challenge” [1]. He ranked the top 10 challenges facing mankind for the coming 50 years and made a compelling argument for energy being the number one challenge, and that it will also dominate the remaining nine challenges (water, food, environment, poverty, terrorism and war, disease, education, democracy, and population). Eleven years into his 50-year prediction, his analysis is holding strong.

The US National Research Council has produced a series of reports about America’s energy future, culminating in the 2009 report *America’s Energy Future: Technology and Transformation* [2]. These reports outline a desirable energy future that is clean, sustainable, and secure, and relies on domestically supplied low-carbon or carbon-free primary energy resources, combined with efficient fuel conversion and end-use technologies. All this may, to a considerable extent, hinge upon technologies to generate, store, distribute, and utilize electricity.

Energy technologies, however, represent only the necessary, but not sufficient, conditions for achieving the above. Sufficient conditions include economics (reasonably well recognized and understood) and a whole host of issues in the societal dimensions, including energy policies, politics, public education and public attitudes, energy security, foreign policy, and even defense. These come together with issues of the environment, ecology, and even climate. The resulting “energy conundrum,” the dimensions of which are inseparable and interactive, has only recently started receiving analytical attention [3].

In spite of the complexity of the energy conundrum, the dominant primary energy resources have been evolving in a remarkably orderly pattern as depicted by the logistic analysis of Gruebler and Nakicenovic [4]. In Figure 1.1, F is the estimated fractional saturation level of a given primary energy resource in a given year, and $1 - F$ represents the remaining potential. Plots of $F/(1 - F)$ for the United States over the years 1800–2000 revealed logistic substitution waves of the primary energy sources, from wood to coal to oil to natural gas to uranium. Although not yet significant in 2000, it is reasonable to expect that renewable energy, such as wind and solar, will eventually start making the next logistic wave.

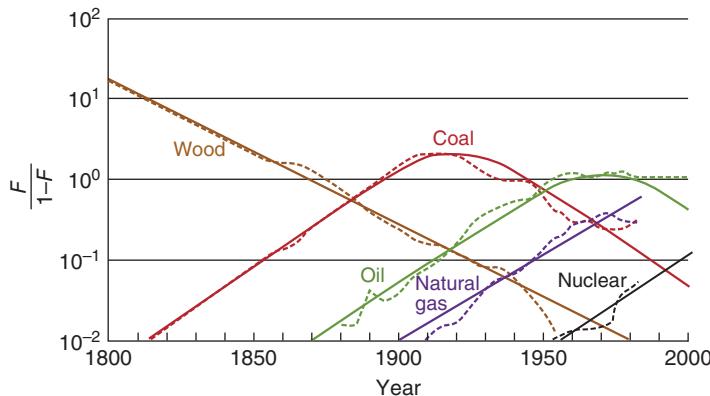


Figure 1.1 Historic logistic wave patterns of the primary energy sources in the United States. (Redrawn from Figure 15 of [2].) F is penetration as a fraction of saturation.

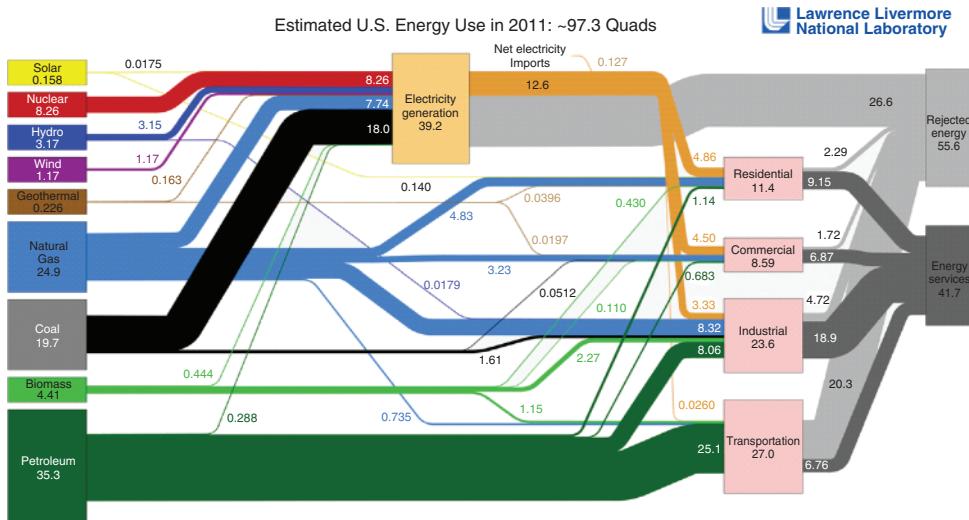


Figure 1.2 Estimated US energy use in 2011. About 40% of the primary energy sources were used for the generation of electricity [3].

The current energy infrastructure in the United States is best visualized by the energy flow charts of the Lawrence Livermore National Laboratory [5]. Figure 1.2 shows that in 2011 (the latest year for which data were available) the United States used about 97.3 quads (10^{15} British thermal units) of energy from our primary energy resources – solar (0.158), nuclear (8.26), hydro (3.17), wind (1.17), geothermal (0.226), natural gas (24.9), coal (19.7), biomass (4.41), and petroleum (35.3). Altogether, 39.2 quads were used for generating 12.6 quads of electricity. One remarkable feature of our energy infrastructure is that almost none of this electricity was used for transportation (0.26%), and another remarkable feature is

that almost none of the natural gas was used for transportation either (inspection reveals that the 3% shown in Figure 1.2 corresponds mostly to the amount of natural gas used to power the compressors of the natural gas pipelines, classified as “transportation”).

Before the historic 18 June 2010 news release of the Potential Gas Committee [6], announcing a 39% one-step upgrade (largely by reclassifying the economic viability of extracting shale gas via horizontal drilling and hydraulic fracturing), the natural gas resources of the United States were viewed as rather limited. Electricity, generated primarily from coal, natural gas, and nuclear resources, was viewed by some as being limited as well: coal due to its environmental, ecological, and climate-change implications; natural gas due to its perceived limited domestic supply, high price, and large price fluctuations; and nuclear resources due to a combination of public safety concerns and the somewhat related high capital costs. The newly perceived natural gas plenty (about 100 years supply at current rates of consumption), and the expectation of low natural gas prices for decades, prompted many existing and planned power plants to shift to natural gas. It has also prompted a re-evaluation of how natural gas and electricity could be used for powering light-duty vehicles instead of oil.

In a 2013 report of the National Research Council [7], projecting technologies suitable for replacing 80% of oil and reducing 80% of CO₂ emissions from the light-duty vehicle fleet by 2050, it was concluded that there will likely be enough natural gas to help electrify light-duty vehicle transportation. (Other ways of using natural gas for vehicle propulsion include converting it into liquid synthetic fuels such as gasoline, diesel, and methanol; compressed natural gas, liquefied natural gas, or natural gas-derived hydrogen for fuel cells.) Fuel cell vehicles are approaching volume production standards but are still too expensive, and of course they rely on the development of a hydrogen fueling infrastructure.

So what are the leading-edge technical issues within the domain of electrochemical engineering? A recent review of the history, accomplishments, and future potential of the field [8] focuses on electrochemical processes and electrochemical processing. While it does mention fuel cells, it leaves batteries unmentioned.

A broader view of the field was represented by a 2007 assessment of US electrochemical engineering research competencies as part of the international benchmarking of US chemical engineering competencies [9]. The study makes observation of the fact that electrochemical engineering has drifted out of the core of the chemical engineering curriculum, with the exception of a handful of leading universities. Among the most notable developments in the field over the previous 10 years were the advances in rechargeable Li ion batteries with liquid, gel, or polymer electrolytes and advances in fuel cells with proton-conducting membranes. For the future, the report projects “increased relevance of the field again, due in part to the world’s repeated energy crises.” Six years after that prediction, we agree.

Electrochemical engineering, similarly to many other engineering disciplines, has been advancing from the scales of macro to micro, nano, and molecular. This increasing overlap in scale with the molecular sciences has become a major

stimulus to both, and the catalyst for much recent progress. Let us examine this thought through the example of advanced battery technology for electric vehicles.

The electrification of light-duty vehicles via the electric grid has the appeal of relatively affordable infrastructure additions. However, it requires batteries that are safe and affordable, provide high energy density (weight, volume, vehicle range, and cost are all affected), provide high power density (performance), have a long cycle life, rely on the domestic supply of key raw materials that would preferably be recyclable but in any case environmentally acceptable, and, last but by far not least, can be recharged quickly to alleviate the customer's range anxiety. Electric vehicles have a number of strong appeals that include the cost of only a few cents of electricity per mile, no tailpipe emissions, greatly simplified vehicle systems (independently controllable electric motors on each wheel, no exhaust system, flexible battery packaging), and startling acceleration due to the fact that an electric motor has its full rated torque at 0 rpm vs. an internal combustion engine that has a narrow revolutions-per-minute band in its torque curve.

We are witnessing the rapid penetration of Li ion battery technologies, originally developed for portable electronics, into battery-electric hybrids, plug-in hybrids (such as the Volt) and battery-electric vehicles (such as the Nissan Leaf and the Tesla Model S). Essentially, all the battery price and performance issues listed before have remained active at various levels; thus, intensive research and development work is continuing on Li ion battery technology. In its wake, batteries are being developed with Li metal anodes and solid-state electrolytes (for a combination of high energy density, safety, and high cycle life), with potential game changers on the horizon that might include consumable (rather than rechargeable) Mg or Al anodes with air cathodes (metal–air “fuel cells”), with very large energy density, simple construction, safe aqueous electrolytes, and instant refueling capability; and the rechargeable Li–air battery that has a theoretical volumetric energy density approaching that of gasoline and that appears to be a potentially achievable “holy grail.” The specific energy (weight-specific energy density) of gasoline is about 13 kWh kg^{-1} , of which about 1.7 kWh is available at the wheels after the thermodynamic and frictional losses have been allowed for. In comparison, the specific energy of today's rechargeable Li ion batteries is about 150 Wh kg^{-1} at the cell level, or about 105 Wh kg^{-1} at the battery pack level. A 200-kg Li ion battery pack yields a driving range of about 70 miles [10].

In a critical review of the Li–air battery [10], it was estimated by cell-level calculations that the Li–air battery could have a practical specific energy of about 1000 Wh kg^{-1} (6.7 times that of today's Li ion battery) “if several fundamental challenges can be overcome.” This would increase the range of the electric car to or beyond the range of today's gasoline-powered vehicles.

So what are the fundamental challenges in making the Li–air battery suitable for propelling the electric car, and how can electrochemical engineers contribute to the solutions? As we will see, the problems cover a dynamic range of close to 10^{10} , from a meter (size of the battery pack) all the way to Angstroms, the molecular scale. We will also see that most (but not all) of the technical challenges appear to reside at the nano- and molecular scales.

There are four types of rechargeable Li–air batteries under development, based on their electrolytes: aprotic, aqueous, solid-state, and aprotic–aqueous hybrid. All have Li metal as their preferred anode (negative electrode), and the preferred cathode (positive electrode) is catalyst-impregnated porous carbon.

The Li anode requires a protection layer that has to conduct Li ions, is thin, hole-free, chemically stable, flexible to accommodate volume and shape change, and has a high elastic modulus to suppress dendrite formation.

The cathode (air electrode) presents particular challenges for aprotic systems: besides being electronically conductive, it has to have a high surface area, which requires small pore diameters; good diffusive properties, which require large pore diameters; and a high pore volume to accommodate the insoluble discharge reaction by-product Li peroxide without pore plugging, which impedes the diffusion of O₂ to the electrode's surfaces. Complex multimodal pore structures have been investigated to find an optimum.

Membranes are being developed for aprotic batteries to prevent H₂O from air to enter the cathode of the aprotic battery. The aqueous battery system, in turn, needs membrane technology that selectively transfers OH[–] ions.

Aqueous batteries require a reservoir for the discharge product LiOH·H₂O due to its relatively low saturation concentration in the aqueous electrolyte.

Catalysts are being developed to help both the reduction of O₂ (discharge reaction) levels and the evolution of O₂ (charge reaction) in the cathode system. These would enhance the rate of discharge (specific power) and the rate of charge, respectively.

Both the aprotic and the aqueous electrolytes need to have high Li ion conductivity, temperature stability, and low viscosity. They also have to be reversible (non-reactive) during the charge–discharge cycles. According to Christensen *et al.* [10], a sufficiently reversible aprotic electrolyte has yet to be found.

As we can see from the above, the technical challenges cover a wide range of scales from battery systems through battery packs, battery cells, battery components, micro- and nanoscale component and materials structures, all the way to chemical compositions and molecular entities. Solving these problems requires working simultaneously along two dimensions: one of these is the collaboration between specialists, and the other one is the engagement of engineers whose interests, training, and experience cover the exceptional dynamic range demanded by modern technologies, as exemplified here by the Li–air battery, leading us to the theme of this volume.

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