

Electrochemistry: Past, Present, and Future

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Advances, Challenges, and Long-Term Opportunities of Electrochemistry: Addressing Societal Needs

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It is a privilege to have been asked to open this conference. I thank the organizing committee for the invitation.

My job is to provide a backdrop for the next day and a half. For the 20 minutes or so that I have, the title given to me, “Electrochemistry: Past, Present, and Future,” is comprehensive enough.

By now, I am a pretty senior figure in electrochemistry. It has been 53 years since I joined Allen Bard’s laboratory as a graduate student. Maybe that span is why I am standing here, for I have seen and experienced a lot of science over those years.

But I don’t go back to the beginning of the field.

The science of electrochemistry is usually dated from 1780, with the work of Luigi Galvani in Bologna. You surely know of his experiments with frog’s legs, in which he discovered that muscle contraction is promoted by electricity, and also by contact of the muscle tissue with two different metals. Galvani’s work was followed-up by Alessandro Volta in Pavia, who was especially interested in the electrical behavior of bimetallic systems. In the process of his work, Volta devised the first electrochemical power source—what we would call a battery—in 1799. It became known as the ‘voltaic pile’ and rapidly became a tool of science—a reliable source of electricity in the laboratory. With use of the voltaic pile, electrolysis of water was demonstrated in 1800, and quite a few elements were discovered or first isolated by electrochemical means before 1810. Lithium was first electrodeposited in 1821, providing the first sample of a pure element that we think about often these days. Electrochemistry yielded the first isolations of strong oxidizing and reducing agents, including fluorine, chlorine, and the alkali metals. When reagents like these became available, the synthetic range of chemistry expanded tremendously.

This little story is offered here just to remind you of three things:

- The history of electrochemistry is long. It spans 240 years, almost matching the length of the whole story of modern chemistry.
- Technological applications of electrochemistry arose right away and began with batteries. We have continued working on them for more than 200 years.

- Electrochemistry connects intimately and broadly with fundamental processes of science. This has been true in every age, because electrochemistry links electrical energy with the material world, and because it focuses on a truly central chemical process, electron transfer.

The operational range of electrochemical systems is breathtakingly large. To illustrate, let me quote from the coming third edition of the text, *Electrochemical Methods*:¹

... electrodes can be as large as several square meters or as small as a square nanometer (10^{-18} m²). Current flow may be in the hundreds of thousands of amperes or it may be in the picoamperes. A current might be required to last for nanoseconds or for years, and the timescales of experimental perturbations can extend from the indefinite to nanoseconds. The use of a system may involve no consumption of material, only a few atoms, or massive amounts. In the upper range, for example, the industrial production of metallic aluminum is wholly accomplished in electrochemical cells. The global economy produces about 50 million metric tons annually. The US share of this production (but less than 5% of the global total) still requires several percent of all US electric power production.

With this operational range, one has the latitude to imagine, and to realize, electrochemical systems big enough to support large segments of an advanced economy. Within that range, one can also deftly and delicately investigate new science. Electrochemistry has always been both a technological and a scientific domain.

But it is not easy. To quote, once more, the new edition of *Electrochemical Methods*:

Key events often take place in a tiny fraction of the total volume, typically at or very near metallic surfaces, or perhaps only at rare active sites on surfaces. The reacting molecules or ions must be transported to the locales of reaction, and the processes of transport influence reaction rates. Once a reaction is initiated at an electrode, it can proceed through a mechanism involving almost any kind of chemical step—proton transfer, a change in ligation, elimination, rearrangement, or even subsequent electron transfer—either at the electrode or with other molecules or ions. Reactions at electrodes involve the orbital structures of ions and molecules and the band structures of metals, semiconductors, and insulators. They depend, too, on electrostatics and thermodynamics. Among the domains of chemistry, electrochemistry offers some of the greatest challenges to effective theory and experimental examination; yet, over two centuries of genuine science, a strong base of theory and experimental methodology has been assembled.

A robust science exists, established through 240 years of research. That is what the past has given us. But nearly all of what we know, what we can do experimentally, and what

¹ A. J. Bard, L. R. Faulkner, and H. S. White, “Electrochemical Methods,” 3rd ed., Wiley, Hoboken, NJ, in preparation.

we can treat theoretically is the product of the last three or four decades. In the course of my career, this field has renewed itself at least four times. It is poised now to renew itself again.

That brings us to the present. Compared to the past and future, the present is but a moment—the outcome of the past and the starting point for the future. However, one can interpret the present in different ways, depending on one’s priorities and interests. For this conference, the subtitle is “Addressing Societal Needs,” so let me focus now on what that might mean.

Through successes rooted in science over the past 200 years, nearly everyone on the globe is far healthier than their forebears, is much further from starvation, enjoys vastly greater mobility, and has unprecedented access to culture and opportunity. As a species, we have flourished. There are 8 times more of us now than in Volta’s time, when global population first reached 1 billion.

But, without doubt, humankind confronts fearful challenges. The Earth groans under the load of her human population and its ambitions. Past patterns of expending global resources, as successful as they have been toward improving people’s lives, cannot underlie the future. Science helped to create the challenges of this era, and science is expected to address them.

Electrochemistry can contribute centrally, precisely because it links electrical energy and the material world and because it has an operational scope big enough to support meaningful industrial change.

Toward the critical goal of transforming the energy economy to a sustainable basis, electrochemistry offers the most likely solutions in two areas of great importance: vehicle propulsion and power-grid management.

- Electrification of vehicles reduces the consumption of fossil fuels and lowers the production of greenhouse gases, particulate matter, and ozone precursors. The long-term environmental benefits can be very large. In the end, success rests on electrochemistry, because electrochemistry furnishes the only answer to the requirement for mobile electric power. I will have more to say about this in a moment.
- An electric power grid must deliver power steadily and predictably. At present, the only clean, renewable, scalable electric power sources are wind and solar. Both are unpredictable and intermittent. The key to sizably greater contributions from wind and solar, is to develop practical means for short-term storage of large amounts of electric power—creating the ability to bank excess local power when wind or solar is producing strongly and to release that power to the grid in periods of local underproduction. The best answers to this need are likely to be electrochemical.

These two domains are ripe for progress and present opportunities for tremendous economic and environmental impact. They merit close, sustained attention and investment.

Electrochemistry might also afford other solutions for environmental challenges. Among them might be greener processes for chemical manufacturing and effective capture, or even useful fixation, of CO₂ from waste streams.

Economic contribution from electrochemistry is far from being wholly defined by the challenge of climate change. Quite recent progress in electrochemical power sources has enabled the very broad—and expanding—success of mobile electronic devices and cordless tools. There is ample opportunity for further advances, supporting new products. There is also the opportunity to improve chemical synthesis through processes that are more precise, also leading to new products.

As we think about opportunity—here in this picture of the present—we must not confine ourselves to visions built on current technology, or even on technology at all. Electrochemistry connects electrical energy and the material world. This will always be a most important linkage for human existence. An ambitious, wise society will place a priority on learning all it can about it. A serious program of research in the basic science of electrochemistry is essential to scientific leadership, and, in the end, to the well-being and security of our nation. There is little doubt of fundamental discoveries that will reshape thinking, and that will redefine the possible in ways that we cannot now accurately sketch.

That brings us to the future. Where should we be headed? Where should we invest?

Naturally, one's first reply to those questions is based on opportunities presently perceived. I just went through a set of those, which included all three technical topics to which panels are dedicated in this conference:

- Energy storage
- Energy conversion
- Electrosynthesis

The speakers themselves will give more detailed analysis and advice than I can, but let me offer a few points.

My earlier comments about automotive propulsion, power-grid management, and portable power connect directly to the theme of energy storage. The prior comments were focused on the “why,” but not the “how” or the “what, exactly.” Let me add these points:

- In all three of those industrial areas, there are good batteries, but not good-enough batteries. There are always demands for better economics, better performance, and better safety.
- Existing batteries are adequate for hybrid vehicles and for all-electric, premium-priced, medium-range passenger vehicles. They are not good enough for all-electric mass-market cars, vehicles suitable for intercity driving, or vehicles that offer the advantages of SUVs. There are no effective all-electric packages for heavier-duty vehicles, including long-haul transports, most construction equipment, or even pickup trucks quite yet. (We in Austin, Texas, are curious about all-electric pickup trucks.)
- Fuel cells are attractive for vehicle propulsion, because of the energy density that can be obtained with storable fuels, the ease of recharge, and the fact that

the oxidant need not be carried on board; however, their economics are not yet competitive.

- Battery systems for power-grid management are in the demonstration stage. Practical answers probably exist, but are not yet clearly at hand. The main issues are the enormity of energy that must be accommodated in a practical storage system and the cycle life of the system.

All applications of electrochemical power sources call for research on

- New ideas for batteries and fuel cells with regard to both composition and design.
- Kinetics of critical processes.
- Lifetime-limiting processes in cells and their packaging.

Let us turn now to the themes of energy conversion and electrosynthesis, each motivating one of the panels in this conference. In both areas, progress hinges on better understanding of complex electrode reactions.

Electrocatalysis remains important. We need to know all we can about the details of electrode reactions of key small molecules—H₂, O₂, H₂O, CO₂, CO, N₂, NH₃, CH₄, methanol—especially at electrocatalytic surfaces. Because these molecules and their reactions have been examined for a long time, new work needs new approaches offering new insight. It has long been understood that large scientific and technological payoffs could stem from advances. In fact, payoffs have come. Much more potential remains.

The blossoming of fresh interest in electrosynthesis also creates a value in greater mechanistic knowledge of electrode reactions, especially of those that can lead to synthetic precision.

Among the most promising new directions for electrochemistry—indeed, a likely basis for the next reinvention of the field—is the ability to explore events at atomic-scale electrodes. Impressive recent work has shown that one can carry out catalytic electrochemistry at a single atom or at assemblies of a few atoms of platinum on a non-catalytic surface. Experimentation in this genre could lead to very significant new understanding of catalytic processes, and, perhaps, in other important scientific areas as well.

Let me close with a wish for a wise humility as we think about research in the years ahead. All of us here must know the wry dictum, credited to Niels Bohr: “Prediction is very difficult, especially about the future.” It’s a warning about having too much confidence in one’s assessment of the future.

Things will change. The possible will not be limited, even five years from now, in some way that applies now. Opportunity will be transformed. Some paths now appraised as very attractive will not pan out. Other opportunities, now discounted or even unseen, will emerge. We have all witnessed such things before, and we can be confident that we will see them again.

It is only sensible to invest in the opportunities that we perceive now, especially when they seem to connect with the fearsome problems that our society, and all others, now face.

But let us also be honest with ourselves. What we already know and can refine will not be enough to solve those problems. New discoveries will be required. We cannot know of their nature at this point, and they cannot be scheduled.

Thus, it is more than wise—it is an essential element of policy—to maintain a vigorous, broad-based program of fundamental research in electrochemistry. We must keep learning about how and why reactions happen at electrodes and how we can control events still more deftly and with greater sophistication. This is how we buy a piece of the yet unknowable future. To the generations who follow, and to ourselves, we owe a faithful, comprehensive effort.