

Electrodeposition for Energy Conversion: Electrochemistry over Matter

by Giovanni Zangari

Electrodeposition as a discipline is currently undergoing a transformation, once again extending its reach into new realms of materials synthesis and applications. This should come as no surprise, since already from its beginnings and various times over, discoveries in the field have quickly led to new—and useful—technological applications.

Electrodeposition in its modern manifestation began in 1803, when Luigi Brugnatelli in Pavia reported using the recently invented Volta pile to gild “two large silver medals.” This technique was then perfected and commercialized in England, where by 1840 the Elkingtons controlled the intellectual property and dominated the European market for silverware plating. Electroplating was used mostly for decorative purposes until after the 1850s, when the invention of new electrodeposition chemistries led to a variety of functional coatings such as copper, nickel, zinc, and brass, that increased the lifetime and improved the appearance of the all-metal parts and machining tools that were being manufactured during the industrial revolution. Throughout the next century electroplating was invariably associated with surface finishing for heavy industry and large scale applications requiring improved corrosion and wear resistance.

With the development of electronic devices and the advent of the information revolution, electrodeposition went through a major transition. Between the 1960s and '70s, through-mask plating of magnetic heads was developed and integrated into commercial products by IBM, enabling a previously unthinkable miniaturization and the parallel manufacturing of the most labor-intensive component in magnetic recording systems. Progress in this technology has been instrumental to the continued performance improvement and decrease in cost of magnetic memories and computers. Arguably, an equally important advance in this direction was achieved with the introduction of copper electroplating in the manufacturing of interconnects for integrated circuits. In order to become a clean technology and enter the clean rooms, the electrodeposition community had to disprove the misconception that associates electrodeposition with grimy warehouses and fuming toxic baths. These innovations were made possible in part by the fact that the scientists who developed these technologies were also responsible for taking them through the development and validation stages to commercialization. Similar obstacles to the commercial success of novel electrodeposition processes persist to this day.

Lately, electrodeposition has become increasingly popular and is being extensively used by researchers in disparate fields of inquiry; what exactly is causing such an interest? The process itself is deceptively simple: a conductive surface is immersed into an electrolyte containing ions of the material to be deposited and a voltage is applied across this solid/electrolyte interface, resulting in a charge transfer reaction and film deposition. The driving force for this process is the applied potential, a quantity that can be easily and precisely controlled down to the mV and over time scales as short as one ns. This feature leads to considerable control over the material formation process, its microstructure, and properties. The charge transfer process occurs preferentially at locations

where the energy barrier for charge transfer is lower; selective deposition can therefore be achieved by using lithographic patterns, suitable surface modification, or otherwise localizing the reaction at selected sites. Deposition rate can be varied over a wide range by the applied potential while keeping the temperature near ambient; the mean free path of the adsorbed species before incorporation in the growing material can therefore be tuned correspondingly, leading to highly metastable or to near-equilibrium structures, at will. From the solution side, the arrival rate of the precursor ions onto the substrate is dictated by a combination of diffusion, convection, and migration; by tuning the process parameters and through proper design of the cell geometry it is possible to achieve conformal coverage of complex, even re-entrant surfaces.

The challenge in developing electrodeposition processes today is not the synthesis of a predefined material, but to strike a compromise between the ideal conditions used to produce this material and the commercial feasibility of the process. Other often cited advantages of electrodeposition include the high utilization rate of the raw materials, low energy consumption, little capital investment and ease of implementation. Although the latter two are usually considered an advantage, they are perhaps a double edged sword: they may in fact encourage quick experimentation, thereby relegating the science to the back stage and undermining the efforts of the community to place this technology on par with vacuum/gas/plasma deposition methods.

A snapshot of the activities in electrodeposition today would show a vast and complex landscape, and the necessarily short discussion that can be provided here may not give justice to the strength and diversity of the field. New materials and processes are being developed and integrated in microelectronic manufacturing to provide new functionalities, for example in MEMS, lab-on-a-chip or microfluidic devices. Polymers and biomaterials are electrodeposited for biomedical applications; metal oxides and compound semiconductors are grown electrochemically for electronic or optoelectronic applications. Electrodeposition in new electrolytic media such as ionic liquids or supercritical fluids is being strongly pursued with some success, but unsolved issues still hinder the development of feasible processes. *In situ* studies of atomistic processes in electrodeposition have achieved a high level of sophistication, but they are often limited in providing a bridge between the atomic level events and the processes leading to microstructure formation. Atomistic modeling of the solid/liquid interface can now include the electrochemical potential into electronic structure and reaction kinetics calculations, and we expect that this method may soon be applied to the atomistic description of electrodeposition processes.

Among all these exciting pursuits, we have chosen to focus this issue on the role that electrodeposition may play in the development of sustainable energy conversion technologies, both at the portable and on a global scale. The versatility in materials synthesis, the ability to control material microstructure and morphology, the low energy utilized and the low material

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Oct. 7-12, PRIME 2012
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2013 Spring Meeting
May 12-17, Toronto, ON, Canada

2013 Fall Meeting
Oct. 27-Nov. 1, San Francisco, CA

2014 Spring Meeting
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Zangari
(continued from previous page)

waste are all arguments that favor electrochemical synthesis methods. In addition, the principles governing the scale up of electrodeposition processes are well understood, facilitating the development of large scale manufacturing processes. The Chalkboard column and the three feature articles in this issue exemplify how the advantages discussed above can be utilized in the fabrication of unique devices or components using electrodeposition.

The Chalkboard column by Stickney explains how electrodeposition may exploit the atomic interactions between adatoms and substrate/deposit atoms to limit deposition to one atomic layer, and how this technique can be used to build up, layer by layer, compound semiconductors or metallic materials.

The article by Vukmirovic *et al.* applies the above strategy and similar methods to fabricate novel catalysts with ultra-low Pt loading capable of reducing the cost while vastly enhancing the performance and durability of fuel cells. In addition, the article outlines a process to grow surfactant-free nanostructures, and shows beautifully how surface chemistry can be exploited to tune morphology of the material being electroplated.

The article by Edstrom *et al.* examines how electrodeposition can be used to fabricate micro- and nano-scale batteries. The use of templates or morphology control to form nanostructures with predefined shapes, and the complementary ability to conformally coat high aspect ratio structures are combined to deposit various classes of materials in widely different shapes, providing a one-stop shop to produce portable batteries with much higher energy density per unit area than currently available.

Finally, the paper by Deligianni *et al.* discusses the possibility to use electrodeposition in the production of photovoltaic devices to enhance their performance while decreasing costs. The ability to provide coatings only in selected regions by exploiting its light-induced selectivity, and the potential to scale up the electrodeposition of complex alloys and compounds to large areas, are significant examples of how this technique can be used to produce devices with potentially higher performance at a lower cost.

The ECS Electrodeposition Division promotes dialogue and initiatives centered on the science and technology of present—and future—electrochemical material synthesis methods. In order to be ever more relevant to the electrochemical community at large, we strive to provide innovative symposia and short courses relevant to both academia and industry, and we welcome your suggestions. Electrodeposition, more than ever, is a technology with immense potential that is ready to tackle important materials synthesis problems and to develop the next groundbreaking manufacturing process. ■

About the Author

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