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Molecular Insight into the Electrical Double Layer

by Stephen J. Paddison

It is nearly 80 years since David C. Grahame's review article (*Chemical Reviews* **41**, 441–501, 1947) on the electrical double layer (EDL). This seminal work (with more than 5000 citations) continues to garner substantial interest and serves as an important pedagogical piece for students learning the fundamentals of electrochemistry. At a recent ESC Meeting I had the privilege to listen to yet another talk on the EDL; and so when asked for a topic for a special issue of *Interface*, I suggested that it be centered around the EDL. Hence, this special issue coedited with **Yue Qi** highlights important progress in understanding this fundamental subject along with provocation for pursuing remaining questions.

Grahame wrote in his review that: "The electric double layer is the array of charged particles and oriented dipoles which is thought to exist at every interface." It is interesting that in his definition of the EDL he was careful to declare the uncertainty as to its broad or wide scale existence. Furthermore, he limited the use of the term in his review article to that pertaining to "the array of charges and dipoles between two immiscible media when one is a salt solution." As one would imagine, a substantial body of both experimental and theoretical research has been undertaken over the past eight decades and hence our collective understanding and insight into the EDL is far more extensive than when Grahame reviewed the body of scientific knowledge in 1945.

A brief review of the fundamentals of the origins and characteristics of an EDL will be helpful. Charge at an interface is typically balanced by an opposite (and equal) net charge of mobile ions in the electrolyte. These electrolyte ions are attracted to the charge on the interface but due to entropic effects are dispersed in the solvent (e.g., aqueous or organic) in the vicinity of the interface surface. It is this charge separation in the electrolyte that is referred to as the EDL. The EDL affects many properties, including (but not limited to): interfacial charge transfer, electrode stability, reaction pathways, and reaction kinetics. The charged ions in the electrolyte (i.e., in the solvent) experience repulsion, but not simply that described by Coulomb's law due to the presence of the counter ions in the double layer.

A host of experimental techniques have been utilized in an effort to characterize the EDL. These methods to be useful must be able to discriminate the properties of the EDL from those of the interface. Measurement of voltage and capacitance provide information concerning the double layer in proximity to the electrode or charged interface and its dependence upon the electrolyte. Advanced experimental techniques such as atomic force microscopy (AFM), electrochemical impedance spectroscopy (EIS), X-ray spectroscopy, and in situ infrared and Raman spectroscopy enable direct investigation of the EDL structure and dynamics on a molecular level. These methods, combined with computational modeling, continue to refine the understanding of electrochemical interfaces.

There are, however, several important and as yet unanswered questions that drive current research. These include: the molecular structure of the EDL under non-ideal conditions; electrolyte behavior and polarization at charged interfaces, the relationship between solvent dynamics and electrochemical reactivity, ion confinement and transport when nanostructured and/or nanoporous electrodes are employed, the coupling between the EDL and electrocatalytic reactions, and the validity of continuum theories and the correct treatment of ion interactions.

As indicated above, this special issue of *Interface* features four invited contributions that summarize progress in addressing important aspects of the EDL with theoretical and computation studies.

Qi and coworkers point out the importance of considering the effects of charge-neutral species (e.g., water, organic solvents, etc.) on the formation and the integrity of the EDL. They point to recent and ongoing first principles and classical molecular dynamics simulations as providing a molecular-level description of the structuring and layering of water when it is utilized as the electrolyte. They make the case that charge-neutral species are not passive and as such offer the opportunity to enhance electrochemical synthesis and catalysis.

Wu in his erudite article describes three important discrepancies that persist between the classical EDL as described by Grahame and the circumstances that bring about its emergence in typical electrochemical systems. Wu advocates that statistical mechanical approaches such as classical density functional theory, when coupled with electronic structure calculations, will provide a much more rigorous and realistic description of the EDL.

It is back to fundamentals as they relate to the practicalities of how electrochemical processes and experiments operate and are conducted in the article by Schmickler. He makes a case that as so much of electrochemistry is performed under conditions where the potential of the electrode is kept constant, the applicable thermodynamic potential to utilize in simulations of the system is the surface tension. If the calculations and simulations are performed at constant potential with an appropriate double-layer model, then reasonable estimates of the change in potential that occur during reactions may be computed.

The contribution by Chaudhary and Alexandrov with a provocative title (a seemingly electrochemical adaptation of the title of C. Dickens' famous novel of 1859!) examines the complexities introduced in understanding the EDL when a semiconductor (as opposed to the customary metallic) electrode is utilized. Non-trivial complications occur in both the potential distribution and with the charge carriers with these electrodes. Finally, they point out the important advances that are occurring due to the integration of machine learning DFT–derived force fields to describe and predict the interfaces occurring in current electrochemical devices.

We hope that this special issue will serve as an appetizer and a primer for electrochemists young and old to pursue further understanding and research into this central important phenomenon in electrochemistry: the electrical double layer.

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