J Solid State Electrochem (2011) 15:1697–1698
DOI 10.1007/s10008-010-1205-7

ORIGINAL PAPER

Trends in electrochemical instrumentation and modeling

Keith B. Oldham

Received: 21 September 2010 / Accepted: 21 September 2010 / Published online: 24 October 2010

One advantage—perhaps the only advantage—of growing old is that it lengthens one's perspective of the past. I performed my first electrochemical experiment in the 1940s. There were then the following steps involved:

- Synthesizing the reagents
- Fabricating the electrochemical cell
- Assembling the instrumentation
- Carrying out the experiment
- Recording the data
- Modeling the experiment
- Comparing the model with the data
- Writing the paper

all of which the investigator had to perform personally. How many of these operations are carried out by today's electrochemists? There are exceptions, of course, but for the most part, we purchase our chemicals, electrodes, and cells readymade, and we use sophisticated commercial instruments, often with only the slightest idea of how they work or what their limitations are. Not only electrochemists, but chemists of all stripes, nowadays use instruments—the operating principles of which they only vaguely understand. How many students know how a pH meter works? There are a few instrumentation specialists, of course, but for the most part, our instruments have become like our motor cars and televisions: they are "black boxes", the workings of which are a mystery. Do we need to know? Of course, we can still use and enjoy our cars and TVs without understanding them, but I believe that as scientists, we need to know the principles of the tools we use on a daily basis.

Please understand that I am not decrying advances in electrochemical technology, which have dramatically improved the reproducibility, accuracy, and rapidity with which electrochemical experiments may be performed. However, there are downsides that must be recognized. In the case of electrochemical instrumentation, the trade-offs are as follows:

$$\begin{array}{c} \text{commercial} \\ \text{versus} \\ \text{homemade} \end{array} \left\{ \begin{array}{l} \text{advantages} \left\{ \begin{array}{c} \text{ease} \\ \text{speed} \\ \text{precision} \\ \text{comparability} \end{array} \right. \\ \text{disadvantages} \left\{ \begin{array}{c} \text{lackofunderstanding} \\ \text{innovationstifled} \\ \text{habituation} \end{array} \right. \end{array} \right.$$

Similar considerations apply to the analysis of electrochemical data.

Let me give two examples of what I call "habituation". In the early days of computation, Fourier transformation was an operation that severely taxed the capabilities of computers.

K. B. Oldham (✉)
Trent University,
Peterborough, ON, Canada K9J 7B8
e-mail: KOldham@trentu.ca

Then, the “fast Fourier transform” was invented. It solved the difficulty and was soon used universally, and it still is, even though the FFT is no longer needed! Nowadays, performing Fourier transformation without a special algorithm is a trivial task for any computer. Another example is the three-electrode cell; it is often used in circumstances where a two-electrode cell would be just as satisfactory and much simpler to implement, but who can break the habit?

Consider cyclic voltammetry. Today it is the paramount investigatory technique of electrochemists; so much so that I have encountered some who think that “voltammetry” actually means “cyclic voltammetry”. Why is it used almost universally? One would like to think that electrochemists choose to employ cyclic voltammetry because they have considered the options and decided that it is the best technique to use for their purpose, but I fear that that is seldom the case. Its use has merely become customary because commercial instruments can be relied upon to carry out the electrolysis, because such computer software as “Digisim” and “DigiElch” are able to help in analyzing the data, because it is so well known that no explanation is needed when writing a manuscript, and because journal referees will raise no queries about the technique. I believe it is for reasons such as these, rather than the technique’s innate superiority, that cyclic voltammetry has become the default voltammetric method. In a nutshell, people use it because others do. Cyclic voltammetry has habituated.

My main interest is in modeling electrochemical events, and I fear that modeling is going, or may have already gone, the way of instrumentation. It is becoming the preserve of a few mathematically inclined experts, with the majority being content to rely on commercial packages based on obscure algorithms. Such a trend is clearly discernable, but is it beneficial? Advantages are similar to those provided by commercial instrumentation, but equally, the disadvantages are also similar to those cited above. Ultimately, electrochemists may come to have only a shallow understanding of the processes taking place in their cells. They may even be unwilling to attempt experiments not addressed by the prevailing software. Repeated use of standard techniques will surely habituate them to the status quo.

The dilemma may be summarized in terms of increasing automation. Thus, just as the adoption of commercial instrumentation historically led to an explosion of data collection, but at the price of neglecting the electronic subtleties of data acquisition, the advent of commercial software is now leading to rapid data interpretation, but at the price of deeply misconstruing the underlying mathematics. What an absurd situation!