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Fractional differential equations in electrochemistry

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A B S T R A C T

Electrochemistry was one of the first sciences to benefit from the fractional calculus. Electrodes may be thought of as “transducers” of chemical fluxes into electricity. In a typical electrochemical cell, chemical species, such as ions or dissolved molecules, move towards the electrodes by diffusion. Likewise, other species are liberated into solution by the electrode reaction and diffuse away from the electrode into the bulk solution. It is demonstrated in this paper that the electric current is linearly related to the temporal semiderivative of the concentrations, at the electrode, of the species involved in the electrochemical reaction. More usefully, the semintegral of the current provides immediate access information about concentrations.

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1. Introduction

No new results are presented in this paper, the purpose of which is to describe how fractional differential equations have influenced one important scientific field, electrochemistry. This was not the first scientific discipline to benefit from the fractional calculus, but it was certainly one of the first to reap a sustained harvest of useful concepts and methodologies.

Probably the earliest written mention of fractional differential equations is in a 1695 letter to L’Hôpital from Leibniz [1], who wrote prophetically, “... it follows that

\[
d_{1/2}x = x \sqrt{dx/x}
\]

an apparent paradox, from which one day useful consequences will be drawn.” Well over two centuries had to pass, however, before any scientific or technological applications of fractional differential equations were made. The earliest of these, as far as I am aware, was in the field of rheology, where Gemant [2] postulated that the gulf of mechanical properties between solids and liquids might be spanned by invoking fractional differentiation. In a series of papers [3–6], Scott Blair developed Gemant’s idea, which in essence uses \(d^{\nu}x\) as an adjustable parameter in describing the behaviour of viscoelastics.

In heat dissipation in aerofoils, Meyer appears to have been the first to realize that, in certain geometries, the heat flux density \(j\) could be measured from a time-record of the temperature \(T\) via the equation

\[
j = \frac{1}{\sqrt{\pi}} \frac{d^{1/2}}{dr} T
\]

where \(\kappa\) is the thermal conductivity. Meyer’s work [7] was not followed up, but the principle of his method is essentially similar to the electrochemical usage discussed below, though applied in a totally different field.

2. Electrochemistry primer

Electrochemists study the interaction of electricity with chemical systems. Their attention is directed, more often than not, to an electrode, which is a junction on one side of which there is an electronic conductor, the other side being an ionic conductor. You can think of a typical electrode being the surface of a piece of metal dipped into salty water, but electrodes can be very different from such a simple arrangement. In any meaningful experiment, there must be two (sometimes more) electrodes and the unit comprising these, together with the intervening ionic conductor, is called an electrochemical cell (Fig. 1). Wires connect to each electronic conductor and the experimenter applies a voltage between these; it may be a constant voltage or it may vary with time, for instance it might be an ac voltage. As a result, a current generally flows through the cell. This current almost always varies with time, even if the applied voltage is constant (Ohm’s law is not obeyed). The experimenter, then, knows the applied voltage \(\Delta V(t)\) and measures the resultant current \(I(t)\).
In the cell, electricity flows through the electronic conductors by the motion of electrons. In the ionic conductor, it is the motion of ions that carries the electricity. Positive and negative charges are necessarily present in equal numbers and so, in the ionic conductor, it is the motion of negative charges in one direction, and of positive charges moving in the other direction, that together is responsible for the flow of electricity. Thus electrons move in the electronic conductor and ions move in the ionic conductor. But how does electricity cross the junctions – the electrodes – where the two kinds of conductor meet? The only way in which electricity can steadily flow across an electrode is by virtue of a chemical reaction: that is where the “chemistry” enters electrochemistry.

As we have seen, reactions at electrodes can have considerable chemical complexity. However, for the purpose of discussing principles, it suffices to consider a simple generic anodic reaction, namely

$$S \rightarrow P + ne^- \tag{9}$$

in which a substrate $S$ is converted into a product $P$ on yielding up $n$ electrons. One or both of $S$ and $P$ will be an ion and we imagine both of them to be dissolved in a liquid solvent, such as water. Reaction (4) matches this model exactly.

As the reaction proceeds, a concentration of $P$ will build up at the electrode, whereas the concentration of $S$ will diminish. These changing concentrations, in turn, will cause the transport of $S$ towards, and of $P$ away from, the electrode. There are three transport mechanisms that could play a role in the transport processes but, under the conditions encountered in most electrochemical experiments, only one of these – diffusion – plays a significant role. Delahay [10] placed electrochemical diffusion on a firm mathematical base in the middle of the twentieth century.

Dimensional arguments show that, during an experiment of duration $t_{max}$, the width of the zone within which the initial concentration is significantly perturbed will be of order $\sqrt{Dt_{max}}$. Here $D$ is the diffusivity, or diffusion coefficient, of the diffusing species which, for typical solutes in solvents such as water, has a value close to $1 \times 10^{-9}$ m² s⁻¹ [9]. Seldom do the electrochemical experiments have durations of more than 90 s and therefore the maximum width of the diffusion zone is about

$$\sqrt{Dt_{max}} \approx \sqrt{(1 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}) (90 \text{ s})} = 3 \times 10^{-4} \text{ m} \tag{10}$$

The dimensions of typical electrochemical cells vastly exceed this 0.3 mm value, so there is ample solution within which the original composition remains unchanged. That is, diffusion takes place under effectively semiinfinite conditions and quite independently of what is going on at the second electrode. Moreover, except for so-called ultramicroelectrodes, the diameter of a typical electrode greatly exceeds the distance given in (10), so that negligible error is introduced by assuming the diffusion field to be planar and by ignoring effects at the electrode’s edge.

Thus the transport of substrate $S$ to, and product $P$ from, the electrode occurs under conditions of planar, semiinfinite diffusion and hence takes place in accord with Fick’s laws, the second of which is

$$\frac{1}{L^2} \frac{\partial}{\partial t} c_S(x,t) = \nabla^2 c_S(x,t) = \frac{\partial^2}{\partial x^2} c_S(x,t) \tag{11}$$
in general coordinates and in those appropriate to the present problem. Here \( x \) denotes the distance measured from, and normal to, the electrode and \( t \) is the time measured from the onset of the experiment. \( D_S \) is the diffusivity of the substrate, a constant, and \( c_s \) is its concentration, a function of both \( x \) and \( t \). Conditions under which this partial differential equation is to be solved include

\[
c_c(x,0) = c_s(x \rightarrow \infty, t) = c_s^0
\]

(12)

Here \( c_s^0 \) is the initial concentration of \( S \), which also remains the constant "bulk" concentration remote from the working electrode throughout the experiment. This is an incomplete set of conditions, because the \( x = 0 \) boundary condition is missing. This is determined by \( \Delta E(t) \), the voltage program, which has not been specified.

Nevertheless, some progress can be made towards a solution by Laplace transforming Eq. (11) to

\[
\frac{d^2}{dx^2} \tilde{c}_S(x,s) = \frac{s}{D_S} \tilde{c}_S(x,s) - \frac{c_s^0}{D_S}
\]

(13)

and thereby incorporating the initial condition in (12). One can solve this ordinary differential Eq. (13) in terms of \( w(s) \) and \( w'(s) \), two arbitrary functions of the Laplace variable \( s \):

\[
c_S(x,s) = \frac{c_s^0}{s} + w(s) \exp \left[ -x \sqrt{\frac{s}{D_S}} \right] + w'(s) \exp \left[ x \sqrt{\frac{s}{D_S}} \right]
\]

(14)

One can argue that \( w'(s) \) must be identically zero, as otherwise, the seminfinte boundary condition could not be satisfied. After incorporating this requirement, it is evident that

\[
w(s) = \tilde{c}_S(0,s) - \frac{c_s^0}{s}
\]

(15)

and accordingly

\[
\tilde{c}_S(x,s) = \frac{c_s^0}{s} \left[ 1 - \exp \left[ -x \sqrt{\frac{s}{D_S}} \right] \right] + \tilde{c}_S(0,s) \exp \left[ -x \sqrt{\frac{s}{D_S}} \right]
\]

(16)

follows.

The electric current is proportional to the flux of species \( S \) arriving at the electrode

\[
I(t) = -nFAD_s \frac{d}{dx} \tilde{c}_S(0,t)
\]

(17)

Here \( A \) is the electrode area and \( F \) is Faraday’s constant (96,485 C mol\(^{-1}\)). The flux is itself proportional, via Fick’s first law, to the gradient of concentration,

\[
J_S(x,t) = -AD_s \frac{d}{dx} \tilde{c}_S(x,t)
\]

(18)

Combination of the previous two equations leads to

\[
I(t) = nFAD_s \frac{d}{dx} \tilde{c}_S(0,t)
\]

(19)

expressing the current in terms of the substrate’s concentration gradient at the electrode.

Prior to the advent of the fractional calculus, the procedure adopted by electrochemists was to hypothesize, on the basis of a known applied voltage \( \Delta E(t) \), what the surface concentration \( c_S(0,t) \), and thence \( c_S(0,0) \), would be. Thereby Eq. (16) could be made specific, and differentiated with respect to \( x \) so providing the information required by Eqs. (18) and (19). There was no way in which the concentration of \( S \), at the electrode, could be found from the measured current \( I(t) \).

4. The fractional differential equations of electrochemistry

Eq. (14) may be differentiated with respect to \( x \)

\[
\frac{d}{dx} \tilde{c}_S(x,s) = \frac{c_s^0}{s} \sqrt{\frac{s}{D_S}} \exp \left[ -x \sqrt{\frac{s}{D_S}} \right] - \tilde{c}_S(0,s) \sqrt{\frac{s}{D_S}} \exp \left[ -x \sqrt{\frac{s}{D_S}} \right]
\]

(20)

and specialized to the \( x = 0 \) electrode

\[
\frac{d}{dx} \tilde{c}_S(0,s) = \frac{c_s^0}{s} \sqrt{\frac{s}{D_S}} - \tilde{c}_S(0,s) \sqrt{\frac{s}{D_S}}
\]

(21)

Making use of the fractional-operator equivalence [11] of powers of the dummy variable, Eq. (21) may be inverse Laplace transformed to

\[
\frac{d}{dx} \tilde{c}_S(0,t) = \frac{c_s^0}{\sqrt{\pi D_S t}} \exp \left[ -\frac{1}{4D_S t} \right] \tilde{c}_S(0,t)
\]

(22)

This basic result [12], relates the spatial derivative of a concentration at an electrode to its temporal semiderivative.

Combination of Eqs. (19) and (22) now produces a novel expression for the current [13]

\[
I(t) = nFAD_s \left[ \frac{c_s^0}{\sqrt{\pi t}} \right] \exp \left[ -\frac{1}{4D_S t} \right] \tilde{c}_S(0,t)
\]

(23)

What is significant about this result is that it interrelates concentration and current quite irrespective of the signal \( \Delta E(t) \) in use during the experiment [14].

Even more useful is the outcome of semiintegrating this result to

\[
\frac{d^{-1/2}}{dt^{-1/2}} I(t) = nFAD_s \left[ \frac{c_s^0}{\sqrt{\pi t}} \right] \exp \left[ -\frac{1}{4D_S t} \right] \tilde{c}_S(0,t)
\]

(24)

The semintegral of the electric current and the electrode concentration are seen to be linearly related. The semintegral of the current is such an important quantity that it is given a special symbol

\[
M(t) = \frac{d^{-1/2}}{dt^{-1/2}} I(t)
\]

(25)

It has units of ampere second\(^{1/2}\) or coulomb second\(^{−1/2}\). Tables of semintegrals have been published [15] to aid that fractional operation when the operand is a standard mathematical function of time.

This account has, thus far, concentrated on the substrate \( S \), but similar results apply to the product \( P \) of the electrode reaction. A difference, however, is that there is (usually) no bulk concentration of the product; \( c_P = 0 \). The analogue of Eq. (22) is therefore

\[
\frac{d}{dx} c_P(0,t) = -\frac{1}{\sqrt{4\pi D_P}} dt^{-1/2} c_P(0,t)
\]

(26)

whence

\[
M(t) = nFAD_s c_P(0,t)
\]

(27)

The current semintegral is seen to be proportional to the concentration of the product: at the electrode, a remarkably simple result.

5. A third Fickian law?

Electrochemical interest focuses on conditions at the electrode, but the equation

\[
\sqrt{\frac{D}{4\pi t}} \Delta c + c_s^{1/2} \sqrt{4\pi D} \Delta c = 0 \quad \Delta c = c(x,t) - c(x,0)
\]

(28)

holds at all points in space and at all times. It applies to both \( S \) and \( P \) and, in fact, generally to any diffusing species under planar seminfinte conditions. For these conditions, Eq. (28) is a much more concise representation of the laws of diffusion than in Fick’s second law.

How is Eq. (28) related to Fick’s second law? The latter, under planar diffusion conditions, may be written

\[
D \frac{\partial^2 c}{\partial x^2} \Delta c - \frac{\partial}{\partial t} \Delta c = 0
\]

(29)
and factored into
\[
\left( \sqrt{D} \frac{\partial}{\partial x} - \frac{\partial^1/2}{\partial t^{1/2}} \right) \left( \sqrt{D} \frac{\partial}{\partial x} + \frac{\partial^1/2}{\partial t^{1/2}} \right) \Delta c = 0 \tag{30}
\]

In this formulation, two operators operate sequentially on \( \Delta c \) and generate zero:
\[
\operatorname{Op}_2(\operatorname{Op}_1 \Delta c) = 0 \tag{31}
\]

But we have proved with Eq. (28), that, in fact, the operation \( \operatorname{Op}_1 \) alone is adequate to produce zero. It appears that that this circumstance, in which only one of the two sequential operators is called into play, is characteristic of a semiinfinite boundary condition. Of course, \( \operatorname{Op}_1(\operatorname{Op}_2 \Delta c) = 0 \) is equally acceptable mathematically, but it is nonsensical physically.

6. Conclusion

Though it is subject to restrictions (planar geometry, semiinfinite diffusion field), Eq. (28), a partial fractional differential equation, applies under most of the conditions that electrochemists employ. Its particular advantage is that its first term is (almost) the flux density and that therefore, as exposed in Section 4, semi-integration of the measured electrical current leads directly to the concentration of the substrate and product of the electrode reaction.

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