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# Fractional differential equations in electrochemistry

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ABSTRACT

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 semiintegral of the current provides immediate access information about concentrations.

## 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'Hospital from Leibniz [1], who wrote prophetically, "... it follows that

$$d^{1/2}x = x\sqrt{dx/x} \tag{1}$$

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 $v$, the differintegration order in the temporal operation

$$\frac{d^{v}}{dt^{v}} \tag{2}$$

as an adjustable parameter in describing the behaviour of viscoelastic materials. Quite different in this regard was the application made by Meyer in 1960, in whose work $v$ was fixed at ½. With interest 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

$$j = \frac{1}{\sqrt{\kappa}}\frac{\partial^{1/2}}{\partial t^{1/2}}T \tag{3}$$

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 [8]

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 $\Delta E(t)$ and measures the resultant current $I(t)$.

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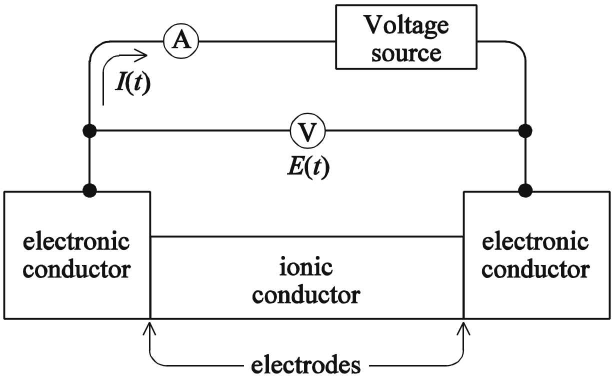

**Fig. 1.** A standard electrochemical cell.

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. Because electrons are involved, these electrode reactions are not ordinary chemical reactions: they are *electrochemical reactions*.

Though there must be two electrodes at which chemistry occurs, interest generally focuses on one of these, known as the *working electrode*. Fig. 2a is a diagram showing a working electrode at which electrons are liberated by the electrochemical reaction. Such a reaction, accompanied by the passage of electrons *into* and through the electronic conductor, is called an anodic reaction or an *oxidation*. Conversely, if electrons come out of the electronic conductor to be consumed at the working electrode, the reaction is described as a cathodic reaction, or a *reduction*, as is illustrated in Fig. 2b. Though an electrochemical reaction must occur, it is not self-evident what that reaction will be. For example, if the electronic conductor is gold (Au) and the ionic conductor is a solution of iron(II) chloride in water, containing the ions $\mathrm{Fe}^{2+}$ and $\mathrm{Cl}^-$ then possible anodic reactions include

$$\mathrm{Fe}^{2+} \rightarrow \mathrm{Fe}^{3+} + \mathrm{e}^- \quad [\text{valency change}] \tag{4}$$

$$2\mathrm{Cl}^- \rightarrow \mathrm{Cl}_2 + 2\mathrm{e}^- \quad [\text{chlorine evolution}] \tag{5}$$

$$6\mathrm{H_2O} \rightarrow 4\mathrm{H_3O}^+ + \mathrm{O}_2 + 4\mathrm{e}^- \quad [\text{solvent decomposition}] \tag{6}$$

$$4\mathrm{H_2O} \rightarrow 2\mathrm{H_3O}^+ + \mathrm{H_2O_2} + 2\mathrm{e}^- \quad [\text{decomposition to a different product}] \tag{7}$$

and

$$\mathrm{Au} + 4\mathrm{Cl}^- \rightarrow \mathrm{AuCl}_4^- + 3\mathrm{e}^- \quad [\text{metal corrosion}] \tag{8}$$

Whichever of these reactions can occur "most easily" will actually happen. Perhaps two of these processes occur simultaneously and possibly the identity of the "easiest" reaction will change with the applied voltage.

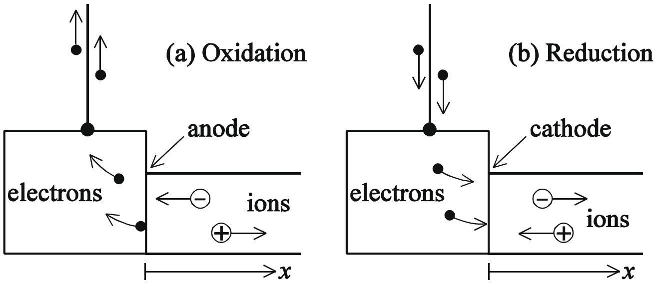

**Fig. 2.** An anode is where oxidation occurs and a cathode is where reduction occurs.

The task of the electrochemist is first to determine which of the competing reactions actually occurs and then to decipher the "why" and "how" of that process quantitatively. Though there are other weapons that can be brought to bear, a major tool is answering these questions is to examine how the current $I(t)$ responds to the applied voltage $\Delta E(t)$. One essential piece of information that is needed to interpret the electrical data, is what the concentration of the various species is at the electrode. It is in the provision of this information that fractional operators prove useful.

## 3. Transport to electrodes

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

$$\mathrm{S} \rightarrow \mathrm{P} + n\mathrm{e}^- \tag{9}$$

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 $1 \times 10^{-9}\ \mathrm{m^2\,s^{-1}}$ [9]. Seldom do the electrochemical experiments have durations of more than 90 s and therefore the maximum width of the diffusion zone is about

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

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

$$\frac{1}{D_\mathrm{S}}\frac{\partial}{\partial t}c_\mathrm{S}(x,t) = \nabla^2 c_\mathrm{S}(x,t) = \frac{\partial^2}{\partial z^2}c_\mathrm{S}(x,t) \tag{11}$$