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Simulated impedance of diffusion in porous media

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ABSTRACT

This paper describes the use of a frequency domain, finite-difference scheme to simulate the impedance spectra of diffusion in porous microstructures. Both open and closed systems are investigated for a range of ideal geometries, as well as some randomly generated synthetic volumes and tomographically derived microstructural data. In many cases, the spectra deviate significantly from the conventional Warburg-type elements typically used to represent diffusion in equivalent circuit analysis. A key finding is that certain microstructures show multiple peaks in the complex plane, which may be misinterpreted as separate electrochemical processes in real impedance data. This is relevant to battery electrode design as the techniques for nano-scale fabrication become more widespread. This simulation tool is provided as an open-source MatLab application and is freely available online as part of the *TauFactor* platform.

1. Introduction

Electrochemical impedance spectroscopy (EIS) is perhaps the most widely used technique for characterising electrochemical devices [1]. Either by fitting equivalent circuit models in the complex plane or by analysis of the distribution of relaxation times (DRT), it is possible to investigate and decouple the relative contributions to the impedance made by the various physical and electrochemical processes occurring in a cell [2].

Although cell electrodes are inherently three dimensional objects, the majority of elements in equivalent circuits (such as resistors, inductors and capacitors) are zero dimensional. Warburg elements are commonly used to model idealised one dimensional diffusion under a variety of boundary constraints. It is possible to find analytical solutions, or reasonable approximations, to many combinations of these boundary scenarios, such as Dirichlet (*i.e.*, specified concentration), Neumann (*i.e.*, specified flux) and semi-infinite [3]. This allows conventional fitting algorithms to incorporate Warburg elements, without the additional computational cost incurred by solving these domains numerically for each set of parameters.

However, the pseudo-1D nature of Warburg elements requires that the intricate details of real 3D microstructures must be summarised with only a few bulk parameters, such as the porosity and tortuosity factor. The tortuosity factor is a measure of the resistance to diffusive transport caused by convolutions in the flow paths [4]. As is shown later in this article, structures with very different morphologies can have identical tortuosity factors and porosities. However, analysing structures across a range of stimulation frequencies, as well as the usual steady-state analysis, enables some additional features of interest to be extracted that may be relevant to performance. Moreover, when analysing impedance data, it would be of interest to know whether the microstructure is responsible for deviations in the spectra away from the conventional Warburg model [5].

The effect of pore geometry on impedance was first modelled in detail in a 1976 paper by Keiser *et al.* [6], following on closely from the work of De Levie [7], where a pseudo-3D numerical model was used to generate impedance spectra for a range of closed pore geometries. The model uses a simplified transmission line assemblage of series resistors and branching capacitors, with the coefficients representing spatial distribution and axi-symmetry. The original paper is in German, but the concept was summarised for a wider audience in a review of EIS methods by Barsoukov and Macdonald [2], which also reframes it in the context of penetration depths. Raistrick [8] points out the limitations of the pseudo-3D approach and Eloot *et al.* [9] do

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question the accuracy and relevance of Keiser's result; however, as these concerns are due in part to the assumptions required to make the calculation computationally feasible under the constraints of the day, it is reasonable to expect that the general trends would still be valid. Although over 40 years have passed since the Keiser paper, the authors of this work were unable to find an instance where the numerical results were directly used in the analysis of an EIS spectrum. This is likely due to both the unavailability of microstructural data and the computational expense of the simulation.

However, despite the uncertainty surrounding the link between EIS spectra and the geometry of microstructures, very many papers have cited Keiser, as well as its subsequent mentions in books and articles by Lasia [10–12], as a possible explanation for distortions in impedance spectra. Malko *et al.* [13] used EIS to investigate PEM carbon catalyst optimisation and attributed a deviation from the expected 45° slope to the pore broadening/narrowing phenomena discussed by Keiser. Noack *et al.* [14] also cited Keiser to explain variation in EIS results between samples of graphite felt electrodes. González-Buch *et al.* [15] used SEM image data to show that the templated pores in their metallic cathodes were narrowing cones, which lead them to conclude that their distorted EIS spectra could be explained by Keiser's findings. A study by Cericola and Spahr [16] analysed the effect of particle size, shape, and orientation on the performance of graphite electrodes and used Keiser's results to interpret a deviation from the expected 90° slope in the low frequency region of a blocked electrode. The degradation of silicon electrodes was investigated by Radvanyi *et al.* [17] and once again, they associate evolution of features in the EIS data to changes in the geometry of the system. A study by Wu *et al.* [18] on supercapacitor electrodes found an additional "arc-shaped" feature in their EIS data which they conclude, citing Keiser, to be the result of transport processes in "orbicular pores", after they systematically rule out other potential causes. Hitz and Lasia modelled "pear-shaped" pores similar to those investigated by Keiser and also observed a semi-cricle at high frequency, rather than the expected 45° slope [11]. As a final remark, Zhang *et al.* [19] highlighted the importance of the pore geometry for designing advanced supercapacitor electrodes, acknowledging that capturing non-uniform ion diffusion is crucial for high power performance. To clarify the cause of variation within the EIS spectra in each of the above cases, the material microstructures must be mapped in 3D and explored.

Recent advances in computed tomography (CT) have allowed the details of porous microstructures to be captured at high resolution [20–23]. This microstructural data is typically stored as cuboid voxels, each containing a grayscale value related to the local density or atomic mass of the sample, depending on the technique used. A segmentation approach must typically then be employed to convert this grayscale data into a labelled volume (although segmentation-free transport simulations are also possible [24]), representing the distribution of the various phases. As demonstrated in many recent studies [25–28], the segmented geometry data can then be used to calculate various microstructural parameters, such as the volume fractions, surface areas, triple phase boundary densities and tortuosity factors; all of which are of interest when trying to predict the performance of, for example, a porous electrochemical electrode

This article presents the implementation of a frequency domain finite-difference solver, suitable for segmented tomographic data, applied to calculate the diffusive impedance spectra of porous materials. First, an investigation of some idealised geometries is presented to aid the intuitive interpretation of the possible effects by analysing several simple open and closed systems. Following this, the method is applied to some real geometries, derived from tomographic data.

2. Method

2.1. Simulation

The solver used in this study is based on the finite-difference approach implemented in the open-source *TauFactor* platform recently released by the authors [24]. *TauFactor* was originally developed for quantifying diffusive tortuosity factors from segmented tomographic data by solving the steady-state diffusion equation between a pair of parallel Dirichlet boundaries. Although it is possible in principle to model a sinusoidal stimulation at one of the boundaries in the time domain, the computational cost would be prohibitive. In this study, the system was transformed into the frequency domain, where a sinusoidal stimulation is once again represented as a Dirichlet boundary condition. This approach allows the various optimization techniques already implemented in the *TauFactor* platform, such as over-relaxation, checkerboarding and vectorisation, to be used in the frequency domain, massively accelerating convergence (for more details, see [24]).

The system of equations in sys. (1) captures this steady-state diffusion problem in the frequency domain, including the fixed value (Dirichlet) conditions imposed at two parallel boundaries, where $Q = (0, L_x) \times (0, L_y) \times (0, L_z)$ is a cuboid in $\mathbb{R}^3$ and $\Omega \subset Q$ is the region of a porous medium inside Q where diffusion occurs. T, I and B are two-dimensional subsets of Q (*i.e.*, Top, Interfacial and Bottom), such that $\partial\Omega = T \cup I \cup B$ and $\partial\Omega|_{z=L_z} = B$, $\partial\Omega|_{z=0} = T$, $\partial\Omega|_{0<z<L_z} = I$. The complex distribution of the diffusing species through the porous medium Ω is then modelled by the solution to

$$\begin{cases} \nabla^2\hat{C} - \dfrac{i\omega}{D}\hat{C} = 0, & \text{in } \Omega, \\ \hat{C} = 0, & \text{on } T, \\ \nabla\hat{C}\cdot\mathbf{n} = 0, & \text{on } I, \\ \hat{C} = 1, & \text{on } B, \end{cases} \tag{1}$$

where $\mathbf{n}$ is the outward pointing unit normal to Ω; $\hat{C}$ is the complex concentration of the diffusing species; i is the imaginary unit; D is the intrinsic diffusivity of transporting phase (set to 1 in all cases); and ω is the frequency of the boundary stimulation, which is changed to calculate each point in a spectrum.

In the case where the top boundary is closed, the condition at boundary T simply becomes the same as boundary I. In all cases, convergence was measured by the stability of the complex impedance measured at the stimulated boundary, B.

In each simulation, a characteristic frequency, ω_c, was defined, around which the frequency range $[\omega_c \times 2^{-4}, \omega_c \times 2^{11}]$ was investigated.

$$\omega_c = \frac{D}{L^2} \tag{2}$$

where, for open systems, L is the length of the control volume (CV) in the direction normal to the stimulated surface and, for closed systems, L is equal to the maximum penetration distance from the stimulated surface to the tip of the longest pore path.

For each frequency, the impedance Z was calculated as the ratio between the amplitude of the concentration stimulus (1 in all cases) and the complex diffusion flux at the inlet boundary, and then normalised to $\tilde{Z}$ for ease of comparison by using Eq. (3).

$$\tilde{Z} = Z\frac{AD}{L} \tag{3}$$

where, for open systems, A is the total area of the CV boundary normal to the direction of flow and, for closed systems, A is the "mean accessible area", which is defined as the algebraic mean area accessible to diffusion at each discrete depth into the pore network. Using this formulation also means that the low frequency