On the use of the constant phase element to understand variation in grain boundary properties

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ABSTRACT

The impedance of polycrystalline electrolytes with heterogeneous grain boundary properties was studied using a two-dimensional numerical simulation. Simulated impedance spectra were generated for samples with random distributions of grain boundary conductivity, permittivity, or both. Equivalent circuit fitting using constant phase elements was then employed to analyze the simulation results with the goal of understanding to what extent such fitting can quantify the average grain boundary parameter values and estimate the spread of these parameters. It was determined that even for quite broad parameter distributions, the mean grain boundary conductivity could be estimated within 30%. The mean grain boundary permittivity could be estimated within 45% using a newly developed empirical expression for effective capacitance. While the degree of heterogeneity of the conductivity and/or permittivity values could be estimated in the case of a single heterogeneous parameter, this was not possible in the case of multiple heterogeneous parameters.

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1. Introduction

Grain boundaries are of great importance in solid-state electrochemical systems, often significantly influencing the overall properties of a sample or device. In polycrystalline electrolytes, for instance, a sizable fraction of the overall DC resistance can often be attributed to grain boundaries [1–4]. In order to distinguish between these grain and grain-boundary effects, the technique of electrochemical impedance spectroscopy (EIS) is often employed [4–6]. Due to the relevant relaxation processes occurring over different frequency ranges, EIS generally allows the grain and grain-boundary impedance contributions to be resolved as separate, roughly semicircular arcs in the complex impedance plane. Coupled with an appropriate model of the electrochemical system, EIS can be used to extract key parameters such as the grain and grain boundary conductivities, permittivities, and dimensions [5,7].

Due to its simplicity, the "brick layer" model is frequently used for this purpose. The brick layer model approximates the electrolyte geometry as a regular array of identical cubic grains separated by grain boundaries of uniform thickness and isotropic, homogeneous material properties [5,7]. This model allows the electrical properties of the electrolyte to be reduced to an analytically solvable equivalent circuit consisting (in the case of grain boundaries that are more resistive than the grains) of two parallel resistor–capacitor (R–C) circuit elements in series (circuit (a) in Fig. 1): one corresponding to the grain and the other to the grain boundary. Fitting of experimental data using this simplified circuit allows the model parameters to be quantified, and

thereby the conductivity and permittivity (and/or thickness) of the grains and grain boundaries to be determined [4,8].

In practice, the idealized brick layer geometry is rarely a good descriptor of actual polycrystals. Real grains can be non-uniform and/or anisotropic in size, shape, and electrical properties [1,9]. Likewise, the grain boundaries are typically geometrically irregular and can have widely varying properties. For example, experimental studies [10–12] have shown that both the conductivity and permittivity of individual grain boundaries can vary significantly within a single polycrystal. Impedance spectra obtained by experiment or by numerical modeling of more "realistic" microstructures [7,13–15] often show impedance arcs that are distorted or depressed (i.e., with a center located below the real axis) rather than ideal semicircles. These impedance responses can suffer from a poor fit using the R–C equivalent circuit. In such cases, an alternate circuit in which each capacitor has been replaced by a constant phase element (CPE) is typically employed (circuit (b) in Fig. 1) [4,14,15].

The CPE is a mathematical generalization of the resistor, capacitor, and inductor elements from classical electrical circuit theory [16] and has an impedance, Z_{CPE}, defined by

$$Z_{CPE} = \frac{1}{Q(i\omega)^n} \tag{1}$$

where $i = \sqrt{-1}$ and ω is the angular frequency. When the exponent n is equal to unity, the CPE represents an ideal capacitor with capacitance Q. In the range $0.7 < n < 1$ the CPE may be thought of as an "imperfect" capacitor, with n providing a measure—albeit one that is rather abstract and of ambiguous physical meaning—of the non-ideality of the device. With the additional parameter n, the R–CPE circuit allows for reduced

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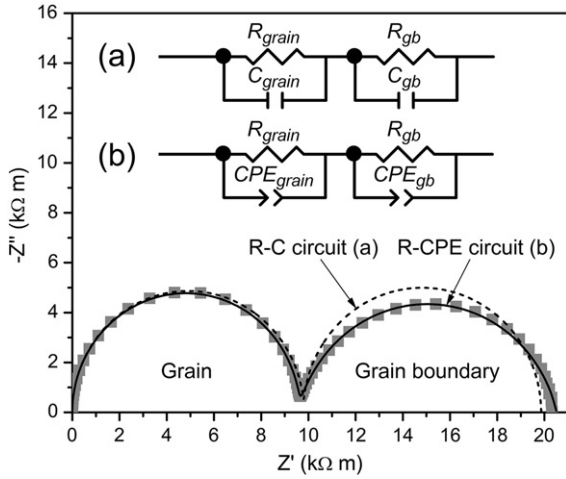E-mail address: bmcnealy@udel.edu (B.E. McNealy).

Fig. 1. Hypothetical impedance spectrum for a polycrystalline electrolyte (squares), along with best-fit curves (dashed and solid lines) corresponding to the indicated equivalent circuits.
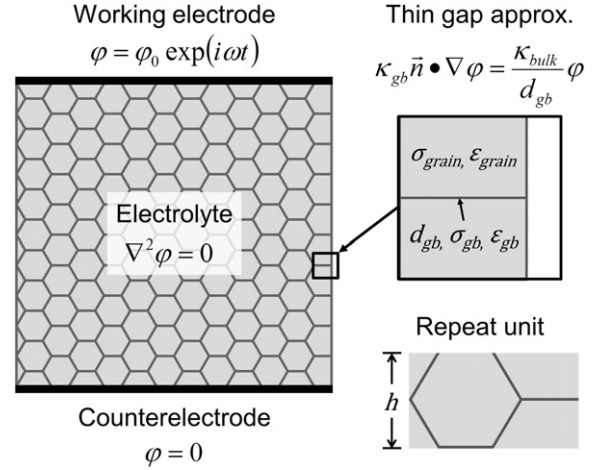

Fig. 2. Schematic of the two-dimensional modeling domain illustrating the polycrystalline electrolyte geometry, key model parameters, and boundary conditions.

residual error in the fit to depressed impedance arcs, as shown in Fig. 1. However, the physical basis for the CPE remains suspect and it remains unclear how best to recover useful information from the CPE parameters Q and n (except in the near-ideal case where simple capacitive behavior is seen).

The relationship between electrolyte microstructure and the resultant impedance spectrum has been studied in detail by Fleig et al. using a numerical modeling approach to solve Laplace's equation over a two- or three-dimensional region with an appropriate treatment of the grain boundaries and electrodes [7,13,14]. This work has shown that a distorted grain boundary impedance arc can result in cases where the grain sizes or electrical properties of the grain boundaries are non-uniform [17,18]. In particular, inhomogeneous grain boundary conductivity was observed to cause distortion of the grain boundary arc. Different numerical distributions of the grain boundary conductivity values were considered, and it was noted that the mean resistance could be satisfactorily estimated using the brick layer model in the case of a relatively narrow distribution. Still, the estimate became quite poor when broader (e.g. uniform or bimodal) distributions were used.

In the present work, the effects of heterogeneous grain boundary properties are investigated in a systematic, quantitative way using numerical modeling. Distributions of not only conductivity but also permittivity, as well as both parameters simultaneously, are considered. A chief topic of interest is to what extent the property distributions can be understood using CPE equivalent circuit fitting. This work will help to clarify the utility of the equivalent circuit parameters in estimating both the average values and the width of the value distributions of grain boundary conductivity and permittivity. Also of interest is how the CPE-type impedance behavior changes with grain size.

2. Methods

2.1. Model framework

In order to generate simulated impedance spectra for arbitrary polycrystalline electrolyte geometries, a two-dimensional, time-domain model was developed using COMSOL Multiphysics (v. 4.3a, COMSOL AB). A schematic of the modeling domain is shown in Fig. 2. Following the method of Fleig et al., the complex electrical potential $\varphi(x,y,t)$ within the electrolyte was obtained by direct numerical solution of Laplace's equation

$$\nabla^2 \varphi = 0 \qquad (2)$$

subject to appropriate internal and external boundary conditions. In arriving at Eq. (2), it was assumed that diffuse space charges can be neglected [19]. The top and bottom boundaries of the electrolyte are in contact with ideally non-polarizable electrodes, between which an AC potential is applied. The potential at the working electrode $(y = Hy)$ was taken as

$$\varphi = \varphi_0 \exp(i\omega t) \qquad (3)$$

where φ_0 is the amplitude of the applied potential. In the present study, φ_0 was set at 20 mV, which is typical of EIS experiments [6]. The counter-electrode $(y = 0)$ was fixed at zero potential, and the free surfaces of the electrolyte were assumed to be perfectly insulating according to

$$\vec{n} \cdot \nabla \varphi = 0. \qquad (4)$$

Once the potential distribution was obtained, the current density distribution was calculated from

$$I = -\kappa \nabla \varphi \qquad (5)$$

with the complex conductivity κ defined as

$$\kappa = \sigma + i\omega\varepsilon\varepsilon_0 \qquad (6)$$

where σ and ε are positive, real values representing the conductivity and relative permittivity, respectively, and ε_0 is the permittivity of free space. The total current (per unit out-of-plane thickness) was then obtained by integrating over an equipotential surface, e.g. the counter-electrode:

$$I_0 = \int_{CE} I \cdot ds. \qquad (7)$$

Finally the complex impedance Z was calculated from

$$Z = \varphi_0 / I_0. \qquad (8)$$

Due to the two-dimensional nature of the electrolyte, the impedance here has units of $\Omega \cdot m$.

The electrolyte microstructure was modeled as an array of uniform hexagonal grains. Unlike the square brick layer geometry, this hexagonal grain structure satisfies the interfacial equilibrium condition in two dimensions and was thus considered to be a better representation of a realistic polycrystal [7,20]. Still, the geometry is simple enough