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Placement of reference electrode in solid state electrolyte cells

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Abstract

A new method is presented for interpreting the data collected using three-electrode configurations, working electrode (WE), counter electrode (CE), and reference electrode (RE) in solid galvanic cells. The common flat arrangement of RE coplanar with the WE, both resting on the solid electrolyte (SE) is experimentally convenient but poses difficulties in the evaluation of the results. A calibration method is presented that allows one to relate the true impedance to the measured signals. It is also shown that in the special case where the RE is placed on a thinner extension of the SE, the placement of the reference electrode side by side introduces only a negligible error. In the case when the current carrying electrodes can be made of equal size, only misaligned, the error can be corrected, to first order, by an averaging procedure, using an annular reference electrode. The configuration analyzed in detail is a 2D one with partial results also reported for a 3D configuration.

Keywords: Reference electrode; Electrode impedance measurement; SOFC; Ionic conductor; Potential distribution

1. Introduction

The placement of reference electrodes in solid state ionic conductors is not as simple as in liquid-state electrochemistry, where the reference electrode can be put into the solution and positioned close to the working electrode. Many of the arrangements used in solids are problematic. They either produce results that are very sensitive to electrode placement and impedance [1–3] change the potential distribution, do not provide a uniform current density and overpotential at the electrode or require delicate patterns liable to fail [4].

In order to solve the problem of measuring electrode impedance in thin, layered SOFCs, generally one measures the WE–RE and RE–CE voltage drops at both dc and high frequency. The high-frequency measurements are assumed not to include the electrode impedance. Thus by subtracting the high-frequency from low-frequency measurements, one may find the electrode impedances alone. However, it has been shown that this simple procedure is prone to various errors listed above. To eliminate these errors we introduce a method for calibrating the corresponding deviations (which originate from imperfect alignment of electrode and a difference in their impedance) [4]. Another solution is to use a configuration for which the current density is rather uniform and the error introduced by deviation from uniformity small. Additionally we introduce an averaging procedure that can cope with errors introduced by imperfectly aligned electrodes provided they are of the same size.

2. Solution by calibration

This procedure is developed for charge transfer impedance. Charge transfer takes place at the electrode boundary, thus at a very thin layer, and is therefore independent of the electrode thickness. The current density is perpendicular to the interface. We here concentrate on samples of rectangular cross section as shown in Fig. 1b, these being disc-shaped samples as shown in Fig. 1a. We imagine that the charge transfer is taking place at the electrode/electrolyte interface. The WE and CE are of equal size but can be shifted by some unknown amount δ. Their impedance can be different as well. We also consider two dimensional samples of the shape given in Fig. 1c. For these not

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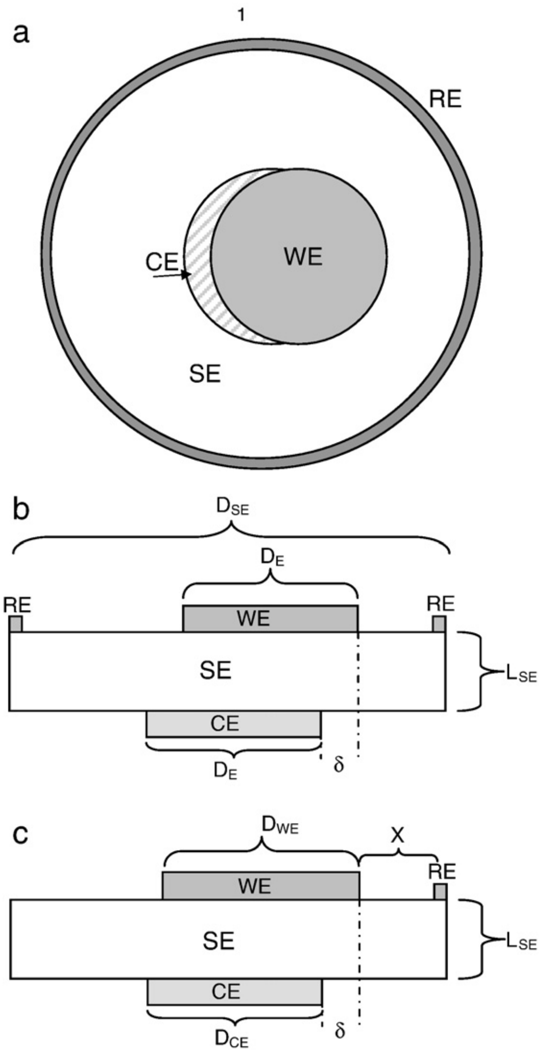

Fig. 1. a — 3D thin circular SE with circular electrodes. WE is displaced with respect to CE which is centered. (The exact position of CE is not important for the thin sample as long as the distance to the periphery is much higher than the thickness). b — Cross section of the 3D sample of (a). c — 2D sample.

only misalignment of WE and CE but also different electrode size is discussed, in addition to different impedance values [4].

The standard, but not necessarily correct, method for determining electrode impedance uses

$$Z_{\mathrm{WE,exp}} = \frac{\eta_{\mathrm{WE,RE.lf}}}{I_{\mathrm{lf}}} - \frac{\eta_{\mathrm{WE,RE.hf}}}{I_{\mathrm{hf}}} \tag{1a}$$

$$Z_{\mathrm{CE,exp}} = \frac{\eta_{\mathrm{CE,RE.lf}}}{I_{\mathrm{lf}}} - \frac{\eta_{\mathrm{CE,RE.hf}}}{I_{\mathrm{hf}}} \tag{1b}$$

where $Z_{\mathrm{WE,exp}}$ is the experimental working electrode (WE) quasi impedance, $\eta_{\mathrm{WE,RE.1f}}$ and $\eta_{\mathrm{WE,RE.hf}}$ are the dc and high-frequency WE overpotentials (voltage drops between working and reference electrode) and similarly $I_{1\mathrm{f}}$ and I_{hf} are the dc and high-frequency currents through the sample. Analogous definitions hold for the counter electrode (CE).

We first present the calibration procedure for the 2D sample [4]. The first step is to determine the misalignment δ between WE and CE (δ is shown in Fig. 1c). This is obtained from the high-frequency overpotential $\eta_{\mathrm{WE,RE.hf}}$ and a calibration curve computed by simulation; see Fig. 2a. It is advantageous to use the parameter δ/L where L is the sample thickness, so that the calibration applies to samples of any thickness (and any size, as long as the electrode width D_{WE} and D_{CE} and the distance X to RE fulfill: D_{WE}, D_{CE}, $X >> L$). Similarly, the parameter $\eta_{\mathrm{WE,RE.hf}}/V_{\mathrm{app}}$ is used in the plot instead of $\eta_{\mathrm{WE,RE.hf}}$ for more general applicability.

For the circular sample, (Fig. 1a and b) the absolute positioning WE and CE is not important as long as they are placed far from the edge where the annular reference electrode is placed. Thus in the simulation CE is kept centered while WE is misplaced, as shown in Fig. 1a and b. The overpotential is measured between WE and RE (or CE and RE) when a highly conductive reference annular electrode is assumed. This annular reference electrode leads to a measured average overpotential. Alternatively, RE may consist of a plurality of small electrodes placed on the periphery of the SE. The overpotential is then measured, for a given current, between an electrode and each of these reference electrodes and the average is calculated. The two averaging procedures (one analogue and one numerical) yield the same results. The measured overpotential is sinusoidal in the angle θ as one travels around the periphery, exhibiting a single period. Thus it is sufficient to determine the average value of the overpotential by measuring only on two small reference electrodes positioned oppositely on the periphery (180° apart). One can determine the direction θ_0 of misalignment of WE vs. CE with respect to three, arbitrary, small reference electrodes equally spaced, located at $\theta_1 = \theta_0$, $\theta_2 = \theta_0 + 120°$ and $\theta_3 = \theta_0 + 240°$ For this we use the equation,

$$\eta_{\mathrm{WE,RE.hf}}(\theta_i) = \overline{\eta}_{\mathrm{WE,RE.hf}} + A\sin(\theta_i), \quad i = 1,2,3. \tag{1}$$

With these three data points one can determine the average value $\overline{\eta}_{\mathrm{WE,RE.hf}}$, the amplitude A and the direction θ_0,

$$\overline{\eta}_{\mathrm{WE,RE.hf}} = \frac{1}{3}\sum_{\theta_i-\theta_0=0,120,240} \eta_{\mathrm{WE,RE.hf}}(\theta_i) \tag{2}$$

and θ_0,

$$\theta_0 = -\tan^{-1}\left(\frac{1}{\sqrt{3}}\frac{2\eta_{\mathrm{WE,RE.hf}}(\theta_1) - \eta_{\mathrm{WE,RE.hf}}(\theta_2) - \eta_{\mathrm{WE,RE.hf}}(\theta_3)}{\eta_{\mathrm{WE,RE.hf}}(\theta_2) - \eta_{\mathrm{WE,RE.hf}}(\theta_3)}\right). \tag{3}$$

The calibration curve $\overline{\eta}_{\mathrm{WE,RE.hf}}$ vs. δ for the sample of Fig. 1a and b is presented in Fig. 2b. $\overline{\eta}_{\mathrm{WE,RE.hf}}$ is quite insensitive to δ and thus cannot be used for determining δ. For a single, small reference electrode instead of an annular one, the calibration curve is different, see Fig. 2c. This curve can be used for determining δ from the measured value of $\eta_{\mathrm{WE,RE.hf}}$. θ_0 is of interest for quality control, as it determines the direction in which the misalignment occurs and thus provides a control parameter for eliminating the misalignment (Optical means are not always applicable as one has to compare the position of two electrodes applied on opposite sides of an opaque SE. This would require a special design of an accurate turn table as sample holder).