Journal of Electroanalytical Chemistry 737 (2015) 65–77

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Current-distribution effects on the impedance of porous electrodes and electrodes covered with films

Morten Tjelta [1], Svein Sunde [*,2]

Department of Materials Science and Engineering, Norwegian University of Science and Technology (NTNU), N-7491 Trondheim, Norway

ARTICLE INFO

Article history:
Received 31 March 2014
Received in revised form 22 September 2014
Accepted 25 September 2014
Available online 8 October 2014

Keywords:
Local impedance
Intercalation
Square
Rectangular
Constant-phase element

ABSTRACT

An analytical formula for the impedance of a disk electrode for general local interfacial impedances has been derived. The formula indicates that the current and potential distributions will affect the impedance data when the measurement frequency is close to or higher than certain critical value. For capacitive or Warburg-like local interfacial impedances, both relevant for porous and intercalation electrode films, the criterion is the same as that previously obtained by Orazem, Tribollet and co-workers through numerical simulation (Huang et al., 2007). Numerical simulation performed here for square and rectangular electrodes show that the criterion will be similar to that for the disk but with the shorter edge length of the electrode playing the role of the disk radius. The local impedances calculated for the square and rectangular electrodes are qualitatively similar to those of the disk. However, for square or rectangular electrodes the current-distribution effects lead to a different appearance in the various plots of the global impedance (impedance-plane plots, Bode plots, etc.) than those for the disk. This is suggested to be due to the "edge-like" and "center-like" local admittances receiving different weight when summed up to the global impedance of the electrode.

1. Introduction

Impedance analysis is indispensable in characterization of electrochemical systems such as faradaic processes at metals [1], capacitance measurements of semiconductor electrodes [2], intercalation in solid or agglomerate films at electrodes [3–8], and rough and porous electrodes [9–12]. For example, electrochemical impedance spectroscopy (EIS) can be used to obtain the potential-capacitance relation which in turn can (ideally) be used to extract the flatband potential of semiconductors, i.e. the potential at which the energy bands become flat, by application of the Mott–Schottky equation [2]. For films on electrode surfaces, such as porous intercalation electrodes used in batteries and battery materials [3,13] and electrochromics [14–16], EIS appears particularly useful since important parameters related to transport and kinetics may be obtained from the data. Several books on EIS have appeared, among them the recent "Electrochemical impedance spectroscopy" authored by Mark Orazem and Bernard Tribollet [17].

While a very powerful technique and more experimentally accessible than ever, impedance analysis is frequently complicated by ambiguities and non-idealities even in the absence of artifacts associated with the collection of experimental data [18]. Fitting of data to equivalent circuits may be useful for a simple assessment of the data in terms of the number of time constants and consistency with Kramers–Kronig relations [19], whereas mathematical models such as those presented in Refs. [3–5,7,8] are desirable for extraction of parameters such as diffusion coefficients and rate constants. However, such mathematical models are usually highly idealized, and deviations from these idealizations may have to be corrected for in the analysis of the data. Vice versa, a model can be employed to guide the experimental work so that such artifacts are avoided in the first place.

Following the seminal work of Newman [20], Orazem, Tribollet and co-workers highlighted in a series of papers the effects of lateral current and potential distributions on the impedance data for disk electrodes [21–23]. For disk electrodes at which the local interfacial impedance at the electrode–solution interface is purely capacitive the global impedance shows deviations from capacitive behavior at high frequencies, and the response is best described through an apparent constant-phase element (CPE) in this frequency range [21]. The CPE, which has an impedance $Z_{CPE} = 1/Q_0(j\omega)^{\alpha}$, was implicitly described by Fricke already in

* Corresponding author. Tel.: +47 735 94051; fax: +47 73 59 11 05.
E-mail address: svein.sunde@material.ntnu.no (S. Sunde).
[1] Current address: Institute for Energy Technology (IFE), Instituttv. 18, NO-2007 Kjeller, Norway.
[2] ISE member.

http://dx.doi.org/10.1016/j.jelechem.2014.09.030
1572-6657/

Nomenclature

List of symbols

a	disk radius, cm
B	coefficients of the series solution, Eq. (12)
$\mathbf{B}$	vector of coefficients B of the series solution, Eq. (25)
B_0	dimensionless current, Eq. (17), Eq. (50)
b_0	dimensionless current density, Eq. (37) or Eq. (47)
c_0	local interfacial capacitance in pore, F cm, Eq. (54)
c	concentration, Eq. (53)
D	diffusion coefficient, cm^2 s^{-1}, Eq. (53)
E	electrode potential, Eq. (53)
F	Faraday number, 96,485 C mol^{-1}
I	total current, A
I	integral, Eq. (19)
$\mathbf{I}$	vector of integral, Eq. (26)
i	current density, A cm^{-2}
J	polarization parameter, Fig. A.2
L	conductance, S
L_x, L_y, L_z	lateral electrode dimensions, m
ℓ	film thickness, m
M_{2n}	Legendre function of imaginary argument, Eq. (14)
P_{2n}	Legendre polynomial of degree $2n$
$\mathbf{P}$	vector of Legendre polynomials
Q	integral, Eq. (24)
Q_0	CPE constant
$\mathbf{Q}$	matrix of integrals Q_{nk}, Eq. (20)
R	gas constant, J mol^{-1} K^{-1}
r_p	resistance in pore, Ω cm^{-1}, Eq. (54)
r	radial coordinate, cm
s	Laplace-variable
T	temperature, K
V	electrode potential, V
w_0	Warburg admittance factor, S cm^{-2}
x, y, z	Cartesian coordinates, cm
Y	global admittance, S cm^{-2} or S
y	local admittance, S cm^{-2}
y_0	local interfacial admittance, S cm^{-2}
Z	global impedance, Ω cm^2 or Ω
z	local impedance, Ω cm^2
z_0	local interfacial impedance, Ω cm^2
z	charge number

Greek

α	CPE exponent
Z	dimensionless global impedance, $1/\Upsilon$
ζ	dimensionless local impedance
κ	electrolyte conductivity, S cm^{-1}
ξ, η, ζ	dimensionless coordinates, Eqs. (4) and (5) or Eqs. (43)
Υ	dimensionless global admittance
υ	dimensionless local admittance
υ_0	dimensionless local interfacial admittance
Φ	solution potential, V
ϕ	dimensionless solution potential, $(zF/RT)\Phi$
χ	dimensionless electrode potential, $(zF/RT)V$
ω	angular frequency, Hz, s^{-1}
Ω	dimensionless angular frequency

Subscripts

i	x, y, or z, Eq. (44)
n, k	index of coefficients B of the series solution, Eq. (12)
$maxY''$	maximum in plots of the logarithm of the admittance vs. Ω
Ω	ohmic

Superscripts

$'$	real part
$''$	imaginary part

Overline

$\sim$	time-dependent part of quantity

Others

$\mathcal{L}\{\}$	Laplace-transform

1932 [24] and later by Cole and Cole [25], but remains elusive. In addition to the effects of lateral current distribution referred to above, observations of impedances with $\alpha \neq 1$ has been discussed in terms of a number of phenomena, such as non-homogeneous surfaces [26], electrode roughness [27–31], adsorption [32], local conductivity variations [33,34], and anomalous diffusion [35], among other things. (Note that a true CPE has a frequency independent α, while the term apparent CPE is used when α is a function of frequency [21].)

The possibility of frequency dispersion at high frequencies for electrodes covered with films due to the effects of current distribution was taken into consideration in Glarum and Marshall's paper [16]. Noting that even for a small capacitive surface "the [electrolyte] resistance leads to a nonuniform current distribution which is manifest in complex plane plots at kilohertz frequencies" they employed a very small electrode of an area of just 0.002 cm^2. Glarum and Marshall [16] did not attempt to specify the frequency range for which such effects would become significant, though.

Current distribution in porous electrodes [9,10] in the direction normal to the electrode may also result in non-integer values for α, and purely capacitive porous electrode may be represented by a CPE with $\alpha = 1/2$. The same type of impedance has been obtained for more complex processes in porous electrodes in the high-frequency limit [6,8,35], and also ion-insertion electrodes will display this type of impedance at high frequencies [7]. For composite electrodes frequency dispersion due to the current distribution effects may even give rise to separate arcs in impedance plane plots [36]. The combined effects of current distribution in the direction normal to the electrode surface in porous and ion-insertion films and lateral current and potential distributions appear to have received little attention in the context of impedance, however.

The object of this work is to investigate the effect of secondary current distribution on the total impedance measured at disk and plate electrodes and to include in the analysis porous electrodes and electrodes covered with electroactive films. We follow the definitions of Ref. [37, pp. 378–396] and refer to the primary current distribution as the current distribution calculated with no surface overpotential (negligible local interfacial impedance) at the electrode and the secondary current distribution as the current distribution when finite surface overpotentials (finite local interfacial impedance) are included. First we derive general impedance models for a disk and a square plate in an insulating plane. Simulations for local interfacial admittances of capacitive or Warburg type[3] are then presented. We will show that both a plate and a disk are influenced above a certain frequency and that the different electrode

[3] We use the term Warburg impedance here referring to its mathematical form, i.e. as an impedance proportional to the square root of $j\omega$, which does not necessarily imply that diffusion in the solution phase is involved.