A Differential Impedance Method for Investigation of Porous Lithium- and Metal Hydride - Battery Electrodes

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Introduction

Usually electrochemical impedance of porous battery electrodes is measured using a reference electrode positioned between the working electrode and the counter electrode (r.e. 1). In this work a reference electrode is also placed at the back of the electrode (r.e. 2) measuring the potential perturbation at the back. As usual the potential perturbation is controlled against r.e. 1. By dividing the measured potential perturbations with the total current, two impedances may be measured, one at the front and one at the back. The additional impedance provides interesting information about both porous character, e.g. potential distribution and electrochemical reactions in the electrode.

Theoretical model

The method used in ref. 1 can be used to derive expressions for the impedance measured with r.e. 1

$$Z_{tot} = R_s + \frac{L}{\kappa_M + \kappa_L} + \frac{1}{\lambda(\kappa_M + \kappa_L)} \cdot \left\{ \frac{1}{\sinh(\lambda L)} + \left[\frac{\kappa_L}{\kappa_M} + \frac{\kappa_M}{\kappa_L} \right] \cdot \coth(\lambda L) \right\}$$

and the impedance measured with r.e. 2

$$Z_{back} = \frac{1}{\lambda \kappa_L} \frac{1}{\sinh(\lambda L)} + \frac{1}{\lambda \kappa_M} \cdot \coth(\lambda L)$$

where λ is expressed as

$$\lambda = \sqrt{\frac{(m \cdot S_a)/(A_e \cdot L)}{Z_{loc}} \cdot \left(\frac{1}{\kappa_L} + \frac{1}{\kappa_M} \right)}$$

and L is the electrode thickness, Z_{loc} is the local impedance function and κ_M and κ_L is the conductivity in the solid and liquid phase respectively (the other parameters with the same meaning as in ref. 1). By forming the difference between these two expressions the differential impedance, Z_{diff}, may be defined.

$$Z_{diff} = Z_{tot} - Z_{back}$$

Results

Impedance spectra was simulated, for a reaction involving diffusion coupled to a charge transfer reaction and varied effective conductivity in the liquid phase and infinite conductivity in the solid phase, Figure 1 (other parameter values typical for the system). The impedance at the front and the back becomes more different the more porous (lower conductivity) the electrode is. Thus, the method gives a graphical representation of the porous character of the electrode, Figure 1.

A major advantage of the method is the clear influence of solid phase conductivity on Z_{diff}. In Figure 2, $-Z_{diff}$ is plotted for different ratios between solid and liquid phase conductivity. It can be seen that for increasing influence of the solid phase conductivity, $-Z_{diff}$ becomes negative at low frequency and when the conductivities are equal the entire curve is flipped. Thus from the study of Z_{diff} it is possible to estimate influence of solid phase conductivity.

A normal fitting procedure may be used for parameter determination and it is believed that this method facilitates the determination of solid and liquid phase conductivity and give stronger test on the correctness of the local impedance expression.

Figure 3 shows the experimentally obtained differential impedance from a porous lithium battery electrode at different temperatures. The electrolyte conductivity decreases with decreasing temperature whereas the solid phase conductivity is almost constant. Thus, the relation, κ_M/κ_L increases with decreasing temperature. As seen $-Z_{diff}$ is negative at high temperatures indicating a solid phase conductivity within the same order as the liquid one whereas at low temperature where κ_M/κ_L is large, $-Z_{diff}$ is positive in agreement with Figure 2. The low frequency behaviour of $-Z_{diff}$ cannot be fully explained but could be related to a mass transfer limitation in the porous electrode.

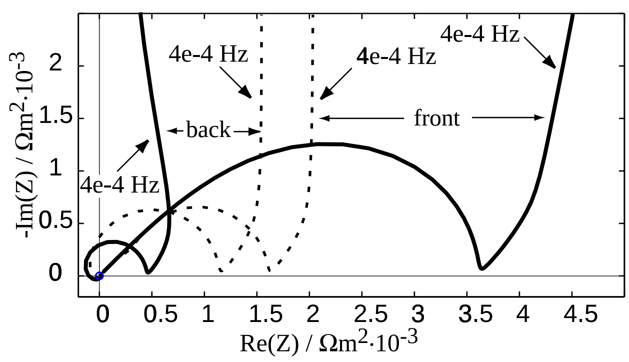

Figure 1 Simulated impedance spectra at the front and the back of the electrode for two different effective conductivities.
- - κ_L=0.2 Sm^{-1}, ━ κ_L=0.02 Sm^{-1}.

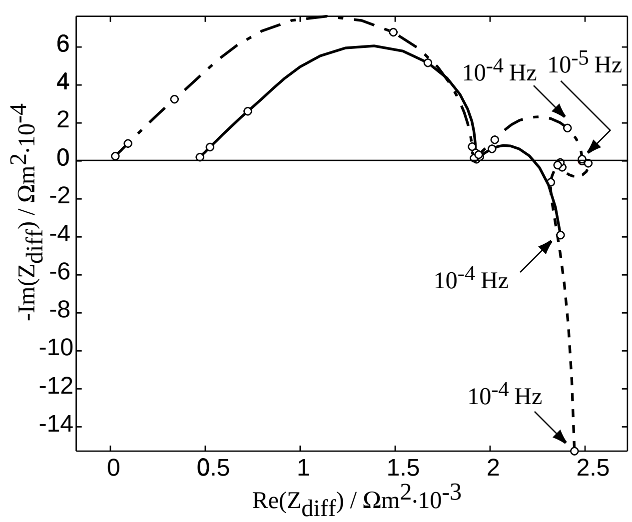

Figure 2 Simulated impedance spectra at the front and the back of the electrode for different relations between conductivity in liquid and solid phases. - — - κ_M/κ_L= inf, ━ κ_M/κ_L= 10, — — κ_M/κ_L= 1

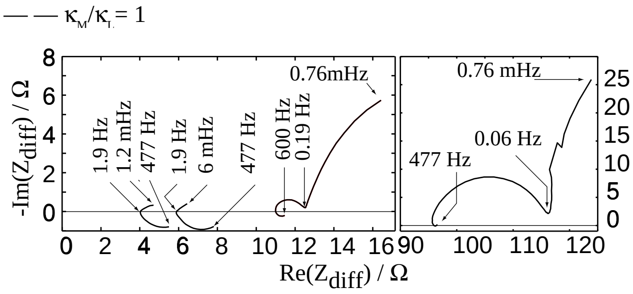

Figure 3 Differential impedance calculated from measurements on a porous lithium battery electrode. Measurements were run at four different temperatures, 54.4°C, 26.6°C, 13.3°C and –0.9°C going from left to right in the figure.

References

1. A. Lundqvist, G. Lindbergh, Electrochim. Acta, **44**, 2523, (1999).