Impedance Spectroscopic Studies of the Porous Structure of Electrodes containing Graphite Materials with Different Particle Size and Shape

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ABSTRACT

The porous structure of graphite electrodes was studied by applying impedance spectroscopy methods to symmetric cells. The electrode structure was varied by changing the particle size distribution and particle shape of the graphite powders used to prepare the electrodes. In addition electrode parameters such as electrode loading, thickness, and density were varied in order identify their effect on the porous structure.

A clear correlation between the equivalent distributed resistance of the symmetric graphite cells and the porosity of an electrode was identified which is independent from the electrode parameters. This correlation is typical for a given graphite type. It was, however, possible to identify a clear trend with the graphite powder particle size distribution and particle shape.

These findings suggest a correlation of the equivalent distributed resistance with the tortuosity of the graphite electrodes. In the case of flaky graphite materials the equivalent distributed resistance increases dramatically with the increase in electrode compaction causing a high tortuosity of the electrode. In the case of bulky or round-shaped graphite materials the equivalent distributed resistance is not much affected by the densification of the electrode which could be explained by smaller electrode tortuosity even at higher electrode density.

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1. Introduction

The porous structure of electrodes has a key role in a number of electrochemical applications including energy storage systems. The porous structure directly affects the flows through an electrode, for example the ionic current in an electrode wetted with an electrolyte, or the gas flows in a gas electrode system. The electrodes used in the majority of electrochemical energy storage devices are based on powder materials; it is therefore likely that the morphological properties of such powders directly determine the porous structure of the electrodes.

In this work we focused on graphite powders which play a key role in several types of electrochemical storage devices [1], and we applied electrode processing and conditions that are normally used in lithium-ion battery technology [2]. Nevertheless the results and conclusions can be transferred to other technologies, in which the electrode porous structure affects the final performance.

The characterization and optimization of the porous structure of graphite electrodes is rather challenging due to the lack of precise characterization methods and detailed studies that correlates the size and shape of the particles with device performance. Gas adsorption methods usually fail as they do not allow the measurement of the pore size range of the graphite electrodes. Mercury intrusion measurements could alter the electrode porosity due to the high applied pressures that are required to characterize the pore size range of the graphite electrodes. Electrode tortuosity measurements by measuring the pressure drop of a gas flow through the electrodes require self-sustaining electrodes without a current collector blocking the permeability of the gas flow.

Impedance spectroscopy is a well-established analysis tool in electrochemistry, and it can be applied to study a number of different systems where the solid electrode/electrolyte interphase is of interest. It can be successfully applied to study porous electrodes/electrolytes either in the case that charge transfer reactions are taking place or not [3].

The impedance response of a porous electrode was initially studied by De Levie who derived a mathematical model applying a transmission line to model the pore [4–6]. The model assumes pores of cylindrical shape of semi-infinite length. Pores should be homogenously filled with the electrolyte and have a uniform distributed resistance and capacitance per unit length. In addition,

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no faradaic reaction should be present; therefore the model considers only capacitive and resistive contributions. Ultimately the impedance of a pore can be described as

$$Z_p = \sqrt{R'Z'}\coth\left(l\sqrt{\frac{R'}{Z'}}\right) \tag{1}$$

Where Z_p is the impedance of a pore, l is the length of the pore, R' and Z' denote the real and imaginary impedance contribution per unit pore length and are defined as

$$R' = \frac{1}{\sigma\pi r^2} \tag{2}$$

$$Z' = \frac{1}{i2\pi\omega rC_S} \tag{3}$$

With r is the pore radius, σ is the electrolyte conductivity, ω is the angular frequency, and C_S is the capacitance per unit area. A porous electrode is constituted by n pores, each one with impedance Z_p. Pores in an electrode, from the electrical point of view, are connected in parallel. An actual electrode, in addition to the pore impedance, has other resistive contributions to the impedance. These contributions are due to a number of factors, and are defined by the *equivalent serial resistance (ESR)*, which for a real electrode account for the electrode material resistance, for the particle to particle contact resistance, for the electrode material to current collector contact resistance, etc. The impedance of a porous electrode (Z_e) can be therefore defined as:

$$Z_e = ESR + \frac{Z_p}{n} \tag{4}$$

The impedance spectrum of a porous electrode calculated according to equation 4 and plotted as a Nyquist plot is reported in Fig. 1. The plot is characterized by the *ESR* which determines the real impedance value of the point at high frequency. The part of the plot at 45°, corresponding to a Warburg [7,8] impedance, is also defined as *equivalent distributed resistance* (*EDR*), which in the case of a porous electrode with only capacitive behavior [9], is followed

by a vertical line. The vertical line in a Nyquist plot is the response of an ideal capacitor.

The analysis of the above-written equations demonstrates that the *EDR* of a porous electrode with a given number of pores increases when the length of the pores increases, or when their radius decreases. In addition, the impedance will also increase when the electrolyte conductivity is reduced. According to equation 4 the number of pores has an impact on the impedance of the electrode and in fact an increase of the number of pores will reduce the *EDR* of the electrode. The *EDR* value represents the effective resistance of the distribute RC network of the porous structure of the electrode [9,3]. Based on this elaboration it is clear that the impedance of a porous electrode in a given electrolyte is determined by a complex balance of number of pores in the electrode, pore length and radius. The electrode resistance at a given frequency is therefore the combination of the *ESR* and *EDR* contributions

The de Levie model was further elaborated by Keiser et al. by introducing the effect of the pore shape [10]. Authors modelled different pore morphologies and demonstrate that for bottle neck type pores the Warburg impedance in the Nyquist plot deviates from 45° towards smaller angles introducing a depression at the knee point. On the opposite, in case of open pores, the Warburg impedance deviates to larger angles leading to a less pronounced knee. Impedance spectra for pear-shaped and spherical pores containing electrodes were simulated by Hitz and Lasia [11]. They also revealed significant deviations for the Warburg impedance towards lower angles for bottlenecked pores.

Beside the rather crude assumption of perfectly cylindrical pores; the de Levie model was demonstrated to be effective in describing the impedance of real electrodes with a complex porous network [12–15]. The tortuosity of the pores defined as the ratio of the length of the pore over the thickness of the electrode can be determined from the analysis of the impedance data [12,16]. Briefly, the experimental length of the pore can be determined from the impedance data. Assuming that the pore passes through the whole electrode, the tortuosity can be estimated by the ratio of the experimental pore length and the electrode thickness. The pore radius and the number of pores are derived from geometrical considerations.

The vertical line in the Nyquist plot, which represents an ideal capacitive behavior, is not always observed in experimental measurements. The low frequency part of the Nyquist plot may deviate from the vertical line towards a line with an angle smaller than 90° with respect to the x-axis. In terms of equivalent circuit this behavior is represented by a constant phase element (CPE) [3]. Considering the porous network, this deviation from the ideal capacitive behavior was explained by implementing the pore size distribution into the de Levie model [17–19]. It was demonstrated that the wider the pore size distribution is, the more pronounced is the deviation.

In this work we report a systematic experimental study of the impedance of a porous graphite electrode at the open circuit potential, with the aim to study and understand the porous structure of the electrode and its correlation with the electrode resistance and graphite particle morphology. In this field, impedance measurements of single electrodes are often done in a three electrode configuration, typically using lithium as reference and as counter electrode. Cell geometry and reference electrode position play a critical role in order to have a reliable measurement, and the risk of having artifacts in the measurements due to the cell setup is high [20]. All measurements reported in this work were measured in a symmetric cell, namely a two electrode cell where the two electrodes are identical. In this configuration, measurements are done at the open circuit potential of the electrode, which for graphite is around 3 V vs Li/Li$^+$. At this potential there are no
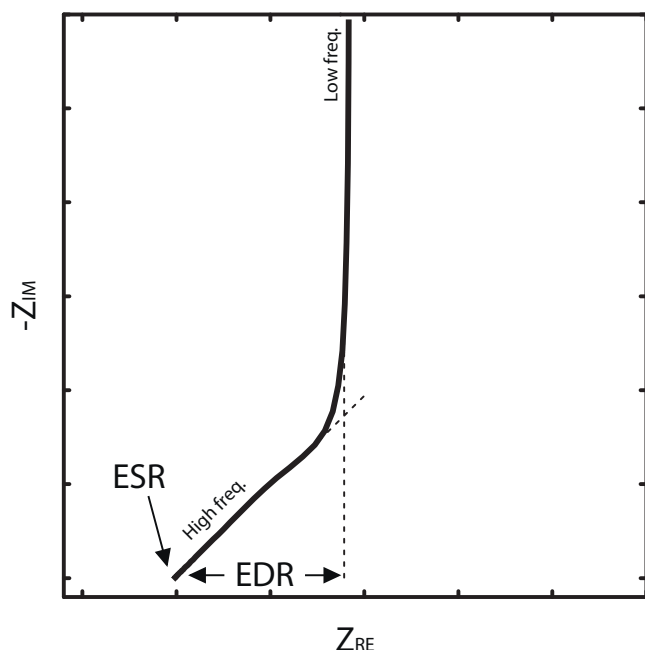

Fig. 1. Nyquist plot calculated according to equation 4.