

Impedance spectra of porous, composite intercalation electrodes: The origin of the low-frequency semicircles

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Abstract

Impedance spectra of composite, graphite electrodes, which are highly porous with a poor orientation of their particles show well-developed low-frequency semicircles (LFSs) with formally very high characteristic capacitances (about 160 mF cm^{-2}), which cannot be rationalized on the basis of the porous electrodes models known from the literature. We use herein a new model (recently reported in full detail) considering two (or more) porous sublayers of different thicknesses, which readily reproduces the well-developed LFSs with very high characteristic capacitances (C_{LFS} in the range from 0.05 to 5 F cm^{-2} using typical values of electrodes parameters, calculated from ω_{max}). A detailed analysis shows that the LFSs characterizing the impedance spectra of highly porous graphite electrodes, have a simple “geometric” meaning. They result from a parallel combination of the intercalation capacitance of the thinnest sublayer and the high, active resistance of the thicker layer. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

Impedance spectroscopy is one of the most important electrochemical techniques, which is widely used for the characterization of Li-ion battery electrodes and even full batteries. While impedance spectra of electrodes always contain highly meaningful and characteristic information, their interpretation is in most cases not trivial and requires very good understanding of all possible processes that occur in the measured systems. A major problem of impedance spectroscopy as an electroanalytical tool is the fact that in most cases, impedance spectra cannot be simulated unambiguously by a single model. Hence, major efforts are invested by prominent electrochemical groups in the development of reliable and comprehensive models that can precisely and logically explain the impedance behavior of electrochemical systems.

Meyers et al. [1] have recently proposed a model for porous electrodes, composed of individual spherical particles with different kinds of particles size distribution (PSD), which represents the basic electrode processes occurring in

Li-ion batteries upon charging and discharging. The modeling is carried out in two steps: (i) firstly, the impedance of a single particle is derived, taking into account the slow, Li-ion transfer through the surface films (so-called solid electrolyte interphase, SEI) around the particle (the characteristic parameters: resistance due to Li-ions migration, R_{sl} , and geometric capacitance of the surface films, C_{sl}); the retarded Li-ion transfer across the SEI/particle interface (the parameters are the charge-transfer resistance, R_{ct} , and the double layer capacitance, C_{dl}), and a finite-space Warburg-type element (specific for spherical particles). (ii) Secondly, the defined impedance of a single particle is incorporated into the expression for the impedance of porous electrodes (composed of host particles which insert Li-ions) with the following four major parameters: the ratio of the true surface area of the particles to their volume, the specific electronic conductivities of the intercalation particles and the solution in the pores space, σ and κ , respectively, and the parameter ψ characterizing the sharpness of the particles distribution.

In a paper published elsewhere [2], we have generalized the Meyers et al. model to the situation frequently occurring with the practical composite electrodes, namely when the active electrode mass covers non-homogeneously the surface

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of the current collector. A simple case is obviously the presence of two porous layers (composed of spherical intercalation particles of two different radii, R_{s1} and R_{s2}), which thicknesses are equal to L_1 (with the fraction θ_1) and L_2 (the corresponding fraction $(1 - \theta_1)$). Usually, impedance spectra of graphite electrodes in the presentation of Nyquist plots comprise two semicircles: high-frequency semicircle (HFS) which relates to Li-ions migration through the surface films that cover the active mass, and a medium-frequency semicircle (MFS) which are usually attributed to charge-transfer of Li-ions across the interface between the surface films and the active mass (R_{ct} , in parallel to an interfacial double layer capacitance, C_{dl}). The implication of this two-layers model is that at certain combinations of the parameters of the porous electrodes structure, a third, low-frequency semicircle (LFS) with formally a very high specific capacitance may appear in the related impedance spectra, in addition to the above mentioned HFS and MFS.

In the present work, we clearly show that the above new model of multilayer, non-homogeneous distribution of the active mass of a porous electrode on its current collector may provide reasonable explanation for the appearance of LFS and the high capacitance values relevant to these LFSs (in the range from a few mF cm^{-2} to several F cm^{-2}). Abundant evidence for the presence of the low-frequency arcs in the impedance spectra of insertion electrodes can be found in recent literature [3–8]. The electroanalytical behavior of porous, composite graphite electrodes containing a non-conductive, non-active methyl silicate binder, prepared by a sol-gel technique [9], is probably a very good example for the verification of models for porous electrodes because they comprise non-oriented particles which form highly porous structure with finite values for the specific electronic and ionic conductivities of the composite structure (κ and σ , respectively).

2. Experimental

The preparation of composite graphite electrodes with a typical mass between 6 and 8 mg (25–30 mm thick), in which the graphite particles (Lonza, KS-6) were embedded into the rigid methyl silicate matrix (MS, 15–25%, w/w) had been described previously [9]. The slurry comprised of graphite powder, methyl-tri-methoxysilane, methanol, HCl catalyst and distilled water was uniformly spread onto a $1.2 \text{ cm} \times 1.2 \text{ cm}$ copper net, and let to be dry over 48 h at ambient temperature (25°C).

Flooded, three-electrode cells with Li counter and reference electrodes were used for slow scan rate cyclic voltammetric (SSCV) and electrochemical impedance spectroscopy (EIS) characterization of thus prepared composite electrodes. The electrolyte solution was 1M LiAsF_6 (Lithco, Li battery grade in a mixture of ethylene carbonate (EC) + dimethylcarbonate (DMC) 1:3, Li-battery grade from Merck, KGaA). Electrochemical measurements were

performed using the Schlumberger 1286 EI and 1255 FRA driven by Corrware and Zplot software from Scribner Association (PC 586).

3. Results and discussion

We have prepared and tested composite graphite electrodes based on a MS binder in the framework of our continuous attempts to look for improved components for Li-ion batteries. It appears that graphite electrodes comprising MS binder are inferior to our conventional electrodes in which we add PVDF as a binder (see later the comparison between some electroanalytical responses). Practical graphite electrodes in Li-ion batteries are usually $100 \mu\text{m}$ thick; they may be composed of different types of particles (e.g. MCMB, chopped carbon fibers, flakes, hard carbon particles, etc.), and show electrochemical characteristics very similar to those of the above-described electrodes comprising MS binder. Hence, we are using herein impedance spectra of these electrodes as suitable reference data, to which we compare calculated impedance spectra, resulting from a refined model of porous electrodes, which we developed [2] based on the previous model of Meyers et al. [1].

Fig. 1 shows SSCV curves for a thin composite graphite electrode comprising synthetic graphite flakes and PVdF (a) and MS (b) binder. Three major cathodic peaks A–C and their anodic conjugates (A'–C') reflect the staged character of Li-ion insertion into graphite matrix as was already discussed [3]. A quantitative comparison between two composite graphite electrodes with PVdF and MS binders of the similar active mass and the thickness reveals broader voltammetric peaks for the latter binder compared to the former one (compare Fig. 1a and b). From the comparison of the electrode's capacity obtained during the first and the subsequent cycles [10], one can conclude that the coverage of the surface of the individual graphite particles with surface films (due to reduction of solution species) proceeds also in a qualitatively similar manner. The most probable reason for the slower kinetics of Li-ion intercalation into a composite graphite electrode with methyl silicate binder compared to that with PVdF binder seems to be a lower electronic conductivity of the composite mass (i.e. a lower specific conductivity σ) in the former case due to a lower contact area between the individual particles. This conclusion is in good agreement with the lower concentration of graphite particles in the former composite electrode and their SEM micrographs, which show lower degree of compactness and orientation [9], compared to that of the electrodes with conventional PVdF binder [3]. It is also probable that the total contact area of the graphite particles with the solution in the porous space surrounding the particles (and hence the specific solution conductivity in the porous volume, κ) is less for the electrode with methyl silicate compared to that with PVdF binder.

Impedance spectra of a graphite electrode comprising MS binder measured at three different potentials in the vicinity

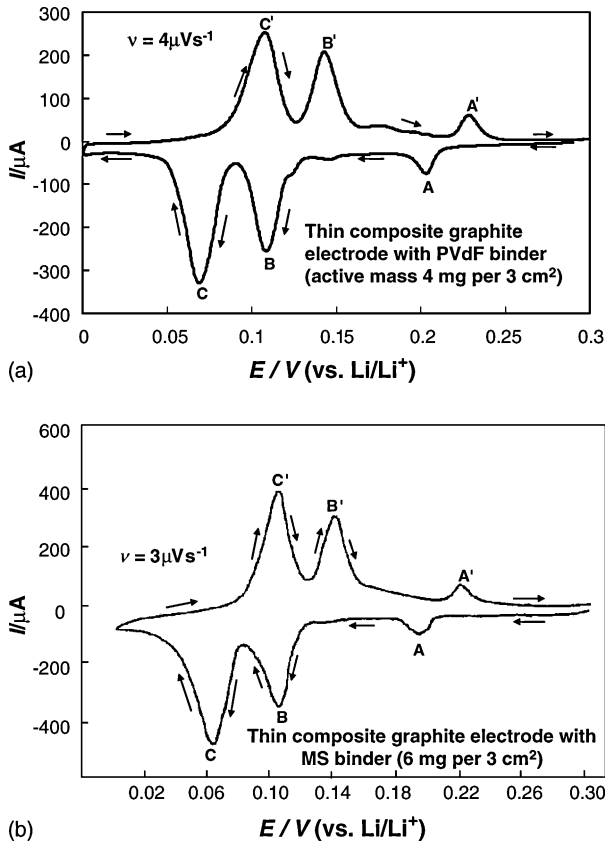


Fig. 1. Slow scan rate cyclic voltammograms measured from a thin composite graphite electrode comprised of PVdF (a) and methyl silicate (MS) binder (b). Letters from A to C and A' to C' designate phase transitions of lithiated graphite during intercalation and deintercalation, respectively. Scan rates as indicated.

of the voltammetric peaks A and B are shown in Fig. 2. Three semicircles with the characteristic frequencies of 790, 25 and 0.16 Hz, designating HFS, MFS and LFS, respectively, are clearly seen in the relevant impedance spectra of the electrode. The characteristic capacitances at the semicircles' maxima were evaluated as 0.005, 1.1 and 60 mF cm⁻² (note, however, that these values relate to 1 cm² of apparent

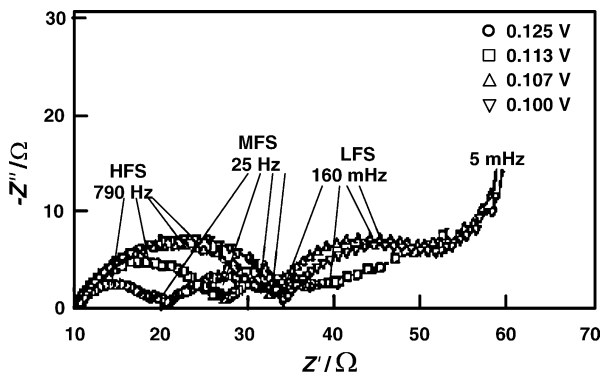


Fig. 2. Nyquist plots measured with a porous composite graphite electrode comprised of MS binder at three characteristic potentials (around the peak B). The characteristic frequencies of the HFS, MFS and LFS are indicated.

surface area of the electrode which is 30 μm thick). Whereas the first two values are well in the range of orders of magnitude of the capacitances expected for the surface films and the double layer, respectively, the capacitance related to the LFS cannot be ascribed to any of the known relaxation processes occurring in the individual graphite particles. Hence, these electrodes provide a good case of impedance spectra containing LFS with high characteristic capacity (as found often for practical thick Li-insertion electrodes).

The origin of the LFS can be qualitatively understood in terms of the model of the inhomogeneously distributed active electrode mass shown in Fig. 3a. For simplicity, only two sublayers L_1 and L_2 thick are considered. Active masses of practical composite electrodes comprise particles of different size, thus for the qualitative consideration we assume that each sublayer is composed of only two particles with the different size (“small” and “large” particles).

The overall impedance of an individual particle, $Z_{\text{part},i}$, can be presented in the following form [1,2]:

$$Z_{\text{part},i} = \frac{R_{\text{ct},i} + \frac{R_{\text{part},i}}{Y_{s,i}}}{1 + j\omega C_{\text{dl},i} \left[R_{\text{ct},i} + \frac{R_{\text{part},i}}{Y_{s,i}} \right]} + \frac{R_{\text{sl},i}}{1 + j\omega R_{\text{sl},i} C_{\text{sl},i}}, \quad (1)$$

with the finite-space diffusion resistive element, $R_{\text{part},i}$, of the form [1,2]:

$$R_{\text{part},i} = \frac{R_{s,i}^2}{3D_s C_{\text{part},i}} = \frac{\tau_i}{3C_{\text{part},i}}. \quad (2a)$$

($1/Y_{s,i}$) is a spherical analog of the characteristic function of angular frequency (ω) in the expression for a linear finite-space Warburg element [1,2]:

$$\frac{1}{Y_{s,i}} = \frac{\tanh(\sqrt{j\omega\tau_i})}{(\sqrt{j\omega\tau_i} - \tanh(\sqrt{j\omega\tau_i}))} \quad (2b)$$

Here, $C_{\text{part},i}$ stands for the limiting low-frequency capacitance of a spherical particle, $R_{s,i}$ the diameter of the spherical particle, D_s the chemical diffusion coefficient, τ_i the related diffusion time constant and ω is the angular frequency of the alternative current. Subscript i denotes particles with different radii, e.g., either 1 or 2. R_{ct} and R_{sl} were defined previously (the diameters of the MFS and HFS, respectively). $C_{\text{dl},i}$ is the interfacial double layer capacitance. The total admittance of an electrode comprising a mixture of two types of particles in terms of different size, $1/Z_{\text{mix}}$, is regarded as an averaged sum of the individual admittances $1/Z_{\text{part},1}$ and $1/Z_{\text{part},2}$ [1,2]:

$$\frac{1}{Z_{\text{mix}}} = \frac{\theta_1}{Z_{\text{part},1}} + \frac{1 - \theta_1}{Z_{\text{part},2}}, \quad (3)$$

where θ_1 is the fraction of the total capacity due to a contribution of the “small” particles (assumed to be 0.5 for further consideration).

The distributed impedance of the porous electrode, Z_{porous} , relates to the impedance of the mixed particles electrode as

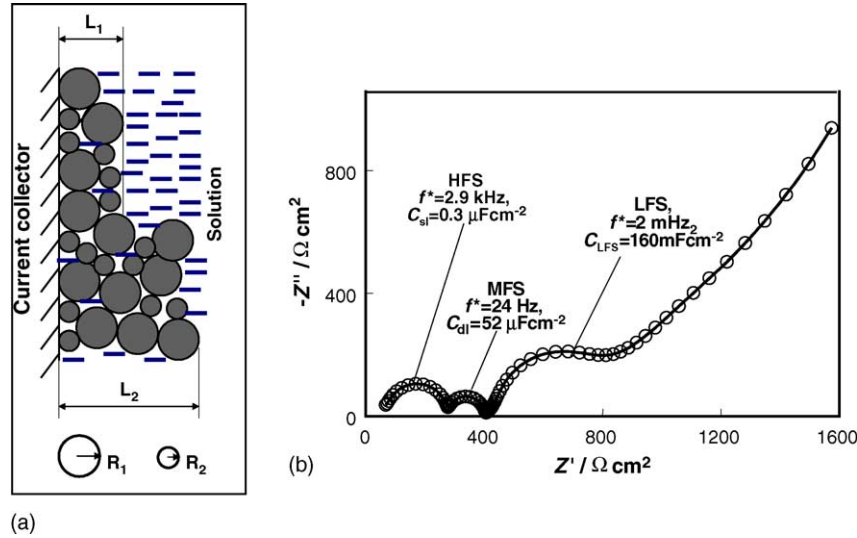


Fig. 3. (a) The model of a simple non-homogeneous coating of current collector with two porous sublayers (thicknesses L_1 and L_2) composed of intercalation particles with two different radii (R_1 and R_2); (b) Nyquist plot calculated according to the model with the use of Eqs. (1)–(6). The following parameters were involved in the calculation. “Large” particles: $R_{s,1} = 4 \mu\text{m}$ ($R_{\text{part}} = 336 \Omega \text{ cm}^2$, $C_{\text{dl}} = 100 \mu\text{F cm}^{-2}$, $R_{\text{ct}} = 88.1 \Omega \text{ cm}^2$, $C_{\text{sl}} = 1 \mu\text{F cm}^{-2}$, $R_{\text{sl}} = 80 \Omega \text{ cm}^2$). “Small” particles: $R_{s,1} = 2 \mu\text{m}$ ($R_{\text{part}} = 84 \Omega \text{ cm}^2$, all other parameters as that for “large” particles). The porous structure parameters: $a = 5 \times 10^3 \text{ cm}^{-1}$, $\kappa = 5.5 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$, $\sigma = 10^{-5} \Omega^{-1} \text{ cm}^{-1}$, $L_1 = 0.04 \text{ cm}$, $L_2 = 0.0003 \text{ cm}$, $\theta_{L_1} = 0.15$ and $\theta_{L_2} = 0.85$.

follows from the model of Meyers et al. [1,2]:

$$Z_{\text{porous}} = \frac{L}{\kappa + \sigma} \left[1 + \frac{2 + ((\sigma/\kappa) + (\kappa/\sigma)) \cosh v}{v \sinh v} \right], \quad (4)$$

with a complex parameter v of the form:

$$v = L \left(\frac{\kappa + \sigma}{\kappa \sigma} \right)^{1/2} \left(\frac{a}{Z_{\text{mix}}} \right)^{1/2}, \quad (5)$$

where κ and σ were earlier defined as the specific conductivities of the electrolyte solution and solid particles, respectively, L the thickness of the porous electrode, a the ratio of the total surface area to its volume and Z_{mix} is obtained from Eq. (3).

The impedance of parallel combination of two porous sublayers (Z_{mix,L_1} and Z_{mix,L_2} are the impedances of two sublayers L_1 and L_2 thick), $Z_{L_1+L_2}$, is given by the formulae similar to Eq. (3):

$$\frac{1}{Z_{L_1+L_2}} = \frac{\theta_{L_1}}{Z_{\text{mix},L_1}} + \frac{1 - \theta_{L_1}}{Z_{\text{mix},L_2}}. \quad (6)$$

In the following modeling, we consider the case when the thicker sublayer, L_2 predominantly cover the surface of the current collector, so that $\theta_{L_2} = 0.85$, thus $\theta_{L_1} = 0.15$ (the general case of the varying ratio θ_{L_1} and θ_{L_2} was analysed elsewhere [2]).

The impedance plot calculated according to Eqs. (1)–(6) (with the numerical parameters indicated in the figure’s caption) is shown in Fig. 3b. This plot reproduces qualitatively all the three semicircles (i.e. HFS, MFS and LFS) characteristic of the experimental impedance spectra of composite graphite electrodes comprising MS binder, which are known to have non-uniform structure (Fig. 2) [9]. The characteris-

tic capacitances related to the HFS may vary (depending on the capacitances of the individual particles selected as the model parameter and the parameters of the porous electrode structure σ and κ) between 0.1 and $10 \mu\text{F cm}^{-2}$, whereas the capacitance related to the MFS varies between 0.01 and 1 mF cm^{-2} . As the dominant sublayer is thick, and the values of σ and κ are low, the capacitances related to the both semicircles of the porous electrode impedance are lower compared to that for the individual particles. On the contrary, with thin electrodes, and high values of σ and κ the impedance spectra exhibit “congruent” behavior with the spectra for the individual particles with a scaling factor related to the true surface area of the porous electrode [1,2].

The most interesting is the origin of the third, LFS and the characteristic capacitances at its maxima. Depending on the parameters used, it may well be found in the range of values from 0.05 to 5 F cm^{-2} . This semicircle is due to a parallel combination of the admittances of two branches (sublayers): a more detailed analysis shows [2] that the intercalation capacitance of the thinner sublayer (covering the surface of a current collector at a relatively low fraction) appears to be in parallel with the dominant, high active resistance of the thicker sublayer. Thus, the appearance of the LFS and the characteristic values of the LFS greatly depends on the fraction of θ_{L_1} , and the values of σ and κ . It should clearly tend to disappear from the impedance spectra of porous electrodes when the porous coating is thin (or) σ and κ have very large values. The model of the parallel combination of two porous sublayers (Eqs. (1)–(6) and Fig. 3b) is in good qualitative agreement with the experimental impedance spectra of composite, porous graphite electrodes with MS binder, which represents a typical case of poorly oriented, porous non-uniform graphite electrodes similar to practical, industrial

graphite electrodes comprising more than one type of particles.

4. Conclusion

Impedance spectra of composite, porous electrodes usually show high and medium-frequency semicircles, which may be characteristic of the dielectric properties of the surface films (C_{sl}) and the electrode's double layer capacitance (C_{dl}), respectively. In some cases (non-oriented electrodes comprising several types of particles) a third, low-frequency semicircle may appear in the spectra. Meyers et al. [1] have proposed a model for porous electrodes with different particles size distribution, which can, in principle, explain the deviation of the values of the characteristic capacitances of the semicircles from the corresponding values, characteristic of the impedance of the individual particles. Previous analysis also revealed that although particle size distribution leads to the appearance of the characteristic low-frequency arc in the impedance spectra of porous electrodes [2], none of the combination of the model parameters leads to well-developed LFS as seen in real spectra. A new model considering two (or more) porous sublayers of different thicknesses may readily reproduce the well-developed LFSs that appear in spectra of non-uniform composite electrodes with very high capacitances at their maxima (from 0.05 to 5 F cm⁻²). A detailed analysis shows that it originates from a parallel combination of the intercalation capacitance of the thinnest sublayer and

the high, active resistance of the thicker layer. The effect is due to finite (not too high) values of σ and κ , and may disappear if these are high quantities. Hence, the presence of thin sublayers in a composite electrode (when it is only a small fraction of the total structure), may lead to the appearance of LFS in the impedance spectra. Hence, appearance of LFS in impedance spectra of porous electrodes indicates non-uniformity and relatively low values of σ and κ . These models predictions are in good qualitative agreement with the impedance spectra of porous graphite electrode containing non-conductive MS binder.

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