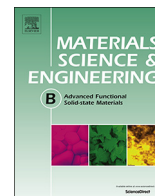




ELSEVIER

Contents lists available at ScienceDirect

Materials Science and Engineering B

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

Interest in broadband dielectric spectroscopy to study the electronic transport in materials for lithium batteries

Jean-Claude Badot ^{a,*}, Bernard Lestriez ^b, Olivier Dubrunfaut ^c^a Institut de Recherche de Chimie Paris, UMR CNRS 8247, Réseau sur le Stockage Electrochimique de l'Energie (RS2E), Chimie Paris Tech, PSL*, 11 rue P. et M. Curie, 75231 Cedex 05 Paris, France^b Institut des Matériaux Jean Rouxel, UMR CNRS 6502, Université de Nantes, 2 rue de la Houssinière, BP32229, 44322 Nantes, France^c GeePs | Group of electrical engineering – Paris, UMR CNRS 8507, CentraleSupélec, Univ. Paris-Sud, Université Paris-Saclay, Sorbonne Universités, UPMC Univ Paris 06, 3 & 11 rue Joliot-Curie, Plateau de Moulon, 91192 Gif-sur-Yvette CEDEX, Paris, France

ARTICLE INFO

Article history:

Received 15 February 2016

Received in revised form 9 May 2016

Accepted 12 May 2016

Available online

Keywords:

Dielectric spectroscopy

Multiscale conductivity and permittivity

Lithium batteries

Composite electrodes

Interfaces

Electronic conductivity

ABSTRACT

Broadband dielectric spectroscopy (BDS) is used to measure complex permittivity and conductivity of conducting materials for lithium batteries at frequencies from a few Hz to several GHz with network and impedance analysers. Under the influence of an electric field, there will be charge density fluctuations in the conductor mainly due to electronic transfer. These fluctuations result in dielectric relaxations for frequencies below 100 GHz. The materials are compacted powders in which each element (particles, agglomerates of particles) can have different sizes and morphologies. In the present review, studies are reported on the influence of surface states in LiNiO₂ (ageing and degradation in air) and LiFePO₄ (carbon coating thin layer), and on a composite electrode based on the lithium trivanadate (Li_{1.1}V₃O₈) active material. The results have shown that the BDS technique is very sensitive to the different scales of materials architectures involved in electronic transport, from interatomic distances to macroscopic sizes.

© 2016 Published by Elsevier B.V.

1. Introduction

Upcoming hybrid electric and pure electric vehicles (HEV and EV) applications require the development of new lithium batteries with high energy density, high power and high cyclability. To reach these goals, a more fundamental understanding of the so called “formulation” of the composite electrode, i.e. the relationships between the processing, the morphology at its different scales, the electrical and mechanical properties and the electrochemical performance of the composite electrode, is needed.

Electronic conductivity is one of the two major electrical properties (the other is the ionic conductivity) of the composite electrode with respect to its electrochemical behaviour. The broadband dielectric spectroscopy (hereafter called BDS) allows the study of the electronic conductivity of a composite electrode at all the scales of its architecture (from interatomic distances to macroscopic lengths) as function of the temperature usually between 200 and 400 K [1–5]. This technique thus allows the clarification of the charge transport mechanisms and the origin of the limitations in these

mechanisms, depending on the composition, processing and morphology of the composite electrode.

Understanding the electrical properties of such hierarchical materials is difficult due to their complexity. First of all, to study each electrode component taken separately is mandatory. We must be aware that the electrical properties of composite electrode are not the sum of all the contributions of its different components taken separately. We must indeed also consider the existence of interfaces (or contacts) at the different levels of the composite electrode: sample/current collector interface, junctions between CB agglomerates, junctions between AM agglomerates, grain boundaries in AM agglomerates, AM/CB interfaces, binder layers (gaps) present at some these interfaces (Fig. 1). The surface effects are thus of the greatest importance to understand the multiscale electronic transfer in composite electrodes.

In the present review, we compare previous studies on the influence of surface states for LiNiO₂ [6] and LiFePO₄ [1,2] active materials. In the first case, the influence of surface ageing and degradation is considered and in the second one, the influence of a carbon coating is analysed. Moreover, the nature of the electronic transfer in composite electrode based on the Li_{1.1}V₃O₈ active material is investigated [4]. Permittivity and conductivity measurements have been recorded in a wide frequency range from 10 Hz to 10 GHz in the temperature range 200 to 300 K.

* Corresponding author. Tel.: +33 1 44 27 80 15.

E-mail address: jc.badot@chimie-paristech.fr (J.-C. Badot).

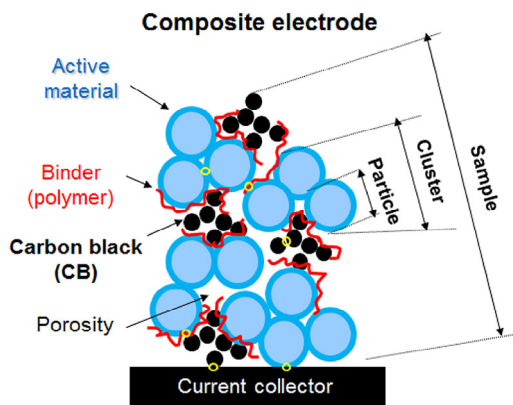


Fig. 1. Schematic representation of a composite electrode.

2. Theoretical background

The electrical response of a material results from charge density fluctuations, when it is submitted to a time-dependent electric field $\vec{E}(t)$. This response is given by a time dependent current density $\vec{J}(t)$ and dielectric displacement $\vec{D}(t)$,

$$\vec{J}(t) = \vec{J}_c + \frac{d\vec{D}(t)}{dt} \quad (1)$$

The first term on the right hand side is the direct current density $\vec{J}_c = \sigma_{dc}\vec{E}$ where σ_{dc} is the direct current conductivity of the material. The second term is the displacement current density $\vec{J}_d = d\vec{D}/dt = \epsilon_0 d(\epsilon\vec{E})/dt$ where ϵ_0 is the vacuum permittivity and ϵ the relative permittivity. In harmonic regime (i.e. $E(t) \propto \exp(i\omega t)$), from equation 1 the relationship between frequency-dependent complex conductivity $\sigma(\omega) = \sigma'(\omega) + i\sigma''(\omega)$ and relative permittivity $\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ can be defined as follows,

$$\sigma(\omega) = \rho(\omega)^{-1} = \sigma_{dc} + i\omega\epsilon_0\epsilon(\omega) = (\sigma_{dc} + \omega\epsilon_0\epsilon''(\omega)) + i\omega\epsilon_0\epsilon'(\omega) \quad (2)$$

The real part of the conductivity is the sum of the DC-conductivity (i.e. at zero frequency) and of a term proportional to the imaginary part ϵ'' (i.e. dielectric losses) of the permittivity (Fig. 2a).

In electronic conductors, several polarization mechanisms occur at different scales (from interatomic to macroscopic sizes) [7] with distinct characteristic frequencies (Fig. 2b). At frequencies below 10^{11} Hz, the dielectric spectra of conducting materials can be generally summarized by the following expression:

$$\epsilon(\omega) = \epsilon_\infty + \left[\sum_m \frac{\epsilon_{mL} - \epsilon_{mH}}{(1 + (i\omega\tau_m)^{1-\alpha_m})^{\beta_m}} \right] + A(i\omega)^{s-1} + \frac{\sigma_{dc}}{i\omega\epsilon_0} \quad (3)$$

where ϵ_∞ is the residual (network) permittivity and A is a fitting parameter. The term in brackets in expression (3) is the sum of m dielectric relaxations described by empirical Havriliak–Negami (HN) functions [8]. For each relaxation, ϵ_{mL} and ϵ_{mH} are the low- and high-frequency limits of the permittivity, τ_m the mean relaxation time; α_m and β_m are fitting parameters. The HN-function is the generalization of the Cole–Cole (CC) function with $\beta_m = 1$, of the Cole–Davidson (CD) function with $\alpha_m = 0$ and of the Debye function (D) with $\alpha_m = 0$ and $\beta_m = 1$ [8]. CC, CD and HN functions result from distributions of relaxation times, which are symmetrical for CC function and asymmetric for CD and HN functions [8]. The Nyquist plots of the complex permittivity (i.e. ϵ'' vs. ϵ') are circular arcs with centres below the ϵ' axis for CC function and skewed arcs for CD and HN function. Note that Nyquist plot of the D function is a semi-circle

centred on the ϵ' axis. Two approaches are considered to interpret the different relaxations: the first one is geometrical and the second is kinetic. In the geometrical approach, when the size of a system increases, its response appears at lower frequency (e.g. agglomerate polarization fluctuates slower than particle polarization). In the kinetic approach, when the mobility of charge carrier increases, its response is shifted to higher frequencies (e.g. ions contributions are generally observed at lower frequencies than the electrons). Consequently, several types of polarizations involving dielectric relaxations can appear from low to high frequencies in the following order: (a) space-charge polarization (low-frequency range) due to the sample/current collector interface; (b) polarization of agglomerates (or clusters) of particles (micronic scale) and (c) polarization of particles due to the existence of resistive junctions between them; d) electron transfers (nanometric or interatomic scale). The resistivity $\rho(\omega)$ and conductivity $\sigma(\omega)$ relaxations also described by the same functions as before are thus given by

$$\rho(\omega) = \rho_H + \frac{\rho_L - \rho_H}{(1 + (i\omega\tau_\rho)^{1-\delta})^\gamma} \quad (4a)$$

$$\sigma(\omega) = \sigma_H - \frac{\sigma_H - \sigma_L}{(1 + (i\omega\tau_\sigma)^{1-\eta})^\kappa} \quad (4b)$$

where the indices L and H mean the low- and high-frequency limits of resistivity and conductivity, τ_ρ and τ_σ the resistivity and conductivity relaxation times; δ , γ , η and κ are fitting parameters similar to those of equation (3).

If we examine the influence of surface effects on the electrical properties, we can consider the two extreme cases most frequently observed: the first one is formed by conducting grains surrounded by a quasi-insulating thin layer (Fig. 3a) and the second one insulating grains surrounded by a conducting thin layer (Fig. 3b). In the first case, the electrical equivalent circuit of the system can be schematized as two parallel combinations of resistance and capacitance in series: the first one is associated with the grains (higher frequencies) and the second with the interfacial region (lower frequencies) (Fig. 3a). The Nyquist plot of the resistivity is the sum of two relaxations often illustrated by two circular arcs (CC functions). The circular arc corresponding to the bulk or grain response crosses the p' axis at the origin when $\nu \rightarrow \infty$. The shape of the conductivity spectrum is similar to a sigmoid curve (Fig. 3a): the low-frequency part (sample conductivity) corresponds to the conductivity of the quasi-insulator phase (σ_s) and the high frequency part to the grain bulk conductivity ($\sigma_g \gg \sigma_s$). In the second case, the interface forms a continuous conducting medium giving rise to a constant conductivity in all the frequency range (Fig. 3b). The Nyquist plot of the resistivity (impedance) shows only one relaxation described by a circular arc (CC function) or a skewed arc (CD or HN function) for highly disordered conducting network (e.g. percolated conductor with concentration slightly higher than the percolation threshold) (Fig. 3b).

3. Experimental devices

The broadband dielectric spectroscopy requires some devices and instruments (network and impedance analysers) for complete coverage of the frequency range. Complex resistivity and permittivity spectra are recorded over a broad frequency range of 40 Hz to 10 GHz, using simultaneously impedance and network analysers Agilent 4294 (40 Hz–110 MHz), 4291 (1 MHz–1.8 GHz), PNA E8364B (10 MHz–10 GHz). The experimental devices, fully described in previous papers [9,10], consists of a coaxial cell (APC7 standard) in which the cylindrically shaped sample fills the gap between the inner conductor and a short circuit (Fig. 4). The samples are powders that are pressed

Download English Version:

<https://daneshyari.com/en/article/5448795>

Download Persian Version:

<https://daneshyari.com/article/5448795>

[Daneshyari.com](https://daneshyari.com)