Short communication

The meaning of impedance measurements of LiFePO$_4$ cathodes: A linearity study

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Abstract

The validity of impedance response measurements within the plateau region of galvanostatic charge–discharge curve of LiFePO$_4$ cathode material was studied in detail. Based on (i) measurement of dependence of impedance response on the mode (voltage, current) and amplitude of excitation, (ii) analysis of higher harmonics of the response signal, and (iii) comparison of impedance response with time-domain measurements, we conclude that above a certain critical frequency that lies in the range 1–100 mHz, the impedance response of LiFePO$_4$ satisfies the criteria of linearity and time invariance (LTI). At lower frequencies the impedance response becomes scattered and does not satisfy the LTI criteria anymore. The critical frequency at which the transition from LTI to non-LTI behaviour occurs, depends on the amplitude of current excitation signal.
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1. Introduction

In numerous studies impedance spectroscopy (IS) has been recognized as a powerful tool for quantitative determination of basic independent transport parameters such as electronic/ionic conductivities and diffusion coefficients [1–3], or for determination of rate constants in electrochemical or coupled electrochemical/chemical reactions [4,5]. As both the transport properties and the electrochemical reactions are of primary interest for any battery system, IS seems to be a natural choice for characterization of various components in battery materials. In reality, however, IS is used quite rarely in lithium battery research, especially if compared to other electrochemical techniques such as galvanostatic measurements, cyclic voltammetry and even galvanostatic or potentiostatic intermittent titration technique (GITT or PITT) that seem to be the preferred methods for determination of chemical diffusion coefficients [6–10].

By contrast, IS is used in a quantitative way in many other fields of electrochemistry. Nice examples of rigorous quantitative treatments are known from the related field of fuel cells [1,2] and even from studies of dissipative electrochemical phenomena, like corrosion [4,5]. A precondition for a quantitative treatment of measured IS spectra is that the system satisfies the criteria of linearity and time invariance (LTI) [11,12]. In the present paper, we study in detail in how far these basic criteria are met in one of the most popular cathode material—LiFePO$_4$.

The charge–discharge kinetics and the accompanying structural changes in LiFePO$_4$ have been extensively researched [13–17]. There seems to be a general consensus that during (slow, reversible) charge of this material, the following main processes occur (Fig. 1): (a) in the first stage (region A), Li is extracted homogeneously from the bulk active material forming a Li-rich solid solution Li$_{1-x}$FePO$_4$. This process results in a Nerstian rise of potential as a function of composition. (b) From ca. $x = 0.89$ to $x = 0.05$ [14], further extraction of Li leads to phase separation into a Li-rich and a Li-poor phase (region B in Fig. 1). As x is increased, the volume of the former decreases and the volume of the latter increases. Kinetically, this can be pictured as movement of phase boundary within a given active particle (see the sketch in Fig. 1). Thermodynamically, a completely constant potential with increasing x is expected in this region. (c) Below $x = 0.05$, Li is gradually extracted from the Li-poor phase (the only remaining phase) until more or less pure FePO$_4$ is obtained. Again, this results in a Nerstian rise of potential as a function of composition (region C in Fig. 1). On lithiation, the reverse processes are expected.

Based on this clear thermodynamic picture one should be able to predict the main features of measured impedance spectra as a function of delithiation/lithiation state. For example,
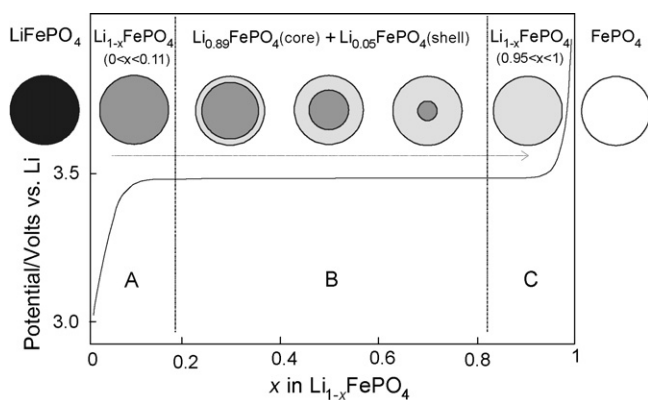

Fig. 1. Schematic presentation of occurrence of various phases during galvanostatic charge (discharge) of LiFePO$_4$ [13,14].

in regions A and C (Fig. 1) the impedance at low frequencies is expected to be dominated by a Warburg impedance due to chemical diffusion of lithium between reflective boundaries, that is, in complex plane one expects to observe an initial slope close to 45° which, at even lower frequencies, turns into a vertical line [11,18]. Different opinions, however, exist as regards the expected impedance behaviour in the constant-potential region (region B in Fig. 1). Some researchers [19] have pointed out at a possibility that impedance measurements in region B could be inherently incorrect ("meaningless") due to the apparently nonlinear nature of the underlying physical–chemical processes (movement of phase boundary between the Li-rich and Li-poor phase). Similarly, Srinivasan and Newman [16] have predicted that interpretation of "experiments..., where the potential is oscillated over a particular state of discharge can be very difficult because of the formation of new shell regions". Finally, taking the thermodynamic picture (Fig. 1) as a starting point, our opinion was that in region B migration of Li, leading to appropriate movement of phase boundary would be the predominating transport mechanism. At low enough frequencies, such a mechanism should yield a purely resistive behaviour, in particular if we assume that the rate-determining step is bulk transport of lithium rather than migration of the phase boundary. Such cases are not unrealistic, examples may be found in IS studies of the Ag/AgCl boundary and in other phase boundaries of the M/MX type [20,21]. In the case of Ag/AgCl boundary it was confirmed undoubtedly that for sample thicknesses ≫ Debye length, the boundary effects in the impedance response are negligible.

To check the actual ac behaviour of Li$_{1-x}$FePO$_4$ in region B, we performed a series of detailed experimental tests. The present paper represents a summary of these tests which can be divided into three categories: (i) dependence of impedance response of Li$_{1-x}$FePO$_4$ on the mode (voltage, current) and amplitude of excitation, (ii) analysis of higher harmonics of response signal, (iii) comparison of impedance response with time-domain measurements.

2. Experimental

As an active material, a well-researched citrate-derived LiFePO$_4$–carbon composite was used [22,23]. In short, iron (III)

citrate (0.03 mol) (Aldrich, 22,897-4) was dissolved in water at 60 °C. Separately, aqueous solution of LiH$_2$PO$_4$ was prepared by dissolving 0.02 mol H$_3$PO$_4$ (Merck 1.00573) and 0.01 mol Li$_3$PO$_4$ (Aldrich, 33,889-3) in water. The solutions were mixed together and the obtained transparent sol was dried at 60 °C to obtain a xerogel.

The electrodes were prepared by spreading the cathode slurry (80 wt.% of as-prepared material + 10 wt.% of acetylene black and 10 wt.% of PVdF in NMP) onto an Al-foil current collector. Circular electrodes with a diameter of 16 mm (2 cm^2) were cut-out from the sheets which corresponded to an active material mass between 7 and 8 mg. The electrodes were dried overnight under vacuum at 110 °C and stored in a glovebox. The electrochemical characteristics were measured in vacuum-sealed triplex foil (coffee bag foil) cells. The electrolyte used was a 1 M solution of LiPF$_6$ in ethyl carbonate/diethyl carbonate (EC:DEC) (1:1 ratio by volume). The working electrode was separated from the counter electrode consisting of metallic lithium with two glass wool separators. Between them a metallic Li strip was inserted serving as a reference electrode. Prior and during the impedance spectroscopy measurements the experimental cell was held at a constant temperature of 60 °C. The impedance spectra were recorded using a Solartron FRA 1260 combined with an EG&G 283 Potentiostat/Galvanostat. The frequency range was 10^6 to 5 × 10^{-5} Hz, the amplitudes used and other conditions are described in Section 3. The analysis of higher harmonics was performed on a Solartron Frequency Response Analyzer (FRA 1250). The galvanostatic measurements were performed using an EG&G 283 Potentiostat/Galvanostat.

3. Results and discussion

Typical impedance responses obtained using voltage excitation signals with two different amplitudes (one with a root-mean-square, rms, amplitude of 5 mV and the other with 100 mV) are shown in Fig. 2a. Before each measurement, the LiFePO$_4$ electrode was charged at a rate of C/20 to 50% (corresponding to a plateau voltage of about 3.45 V) and then equilibrated at open circuit voltage for at least 24 h.

Fig. 2a indicates that the impedance response is more or less independent of amplitude at high enough frequencies (e.g., above ca. 100 mHz) while at very low frequencies (below 100 mHz) the two responses are significantly different. We tried to find reasons for this unexpected behaviour. Based on the thermodynamic picture, we anticipated that at low enough frequencies, each voltage excitation of finite magnitude would drive the system out of region B. To avoid this unwanted complication, we decided to excite the system with a controlled amount of charge, which would always be less than a half of the electrode capacity. This condition is easier to control if we use a current excitation signal (Fig. 2b) instead of the more accustomed voltage excitation. Despite the charge control using a current excitation signal, the two-mode system behaviour is again observed (see Fig. 2b): an amplitude-independent response at moderate and high frequencies and an amplitude-dependent response at low frequencies (typically below 100 mHz, but
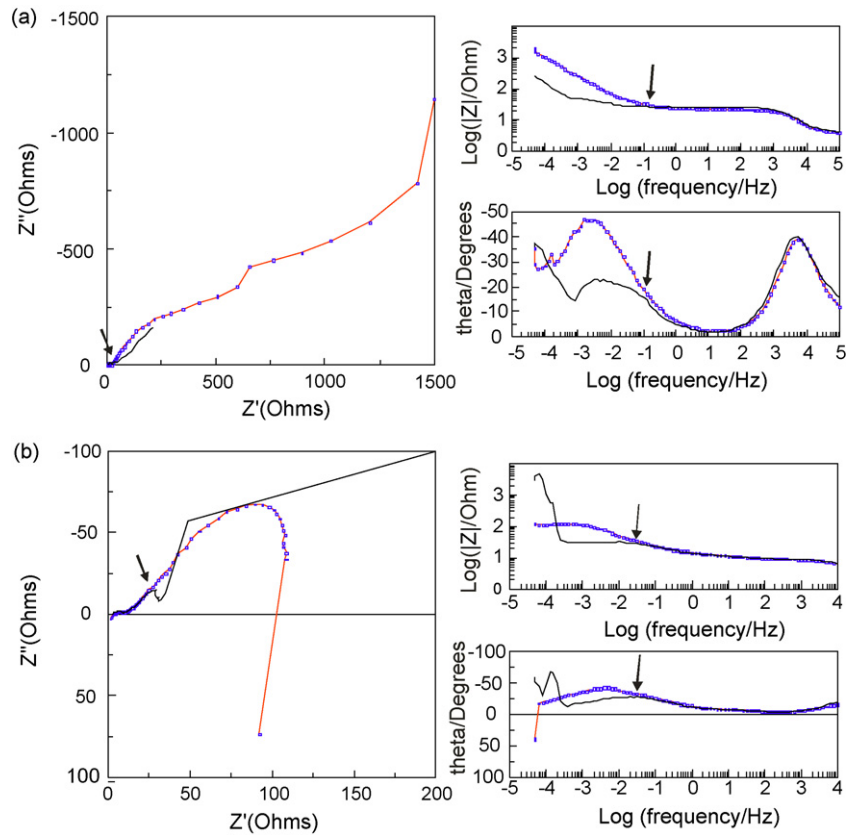
Fig. 2. Impedance responses of a 50% charged sample: (a) voltage excitation: 5 mV (circles + line) and 100 mV (line) and (b) current excitation: 0.1 mA (circles + line) and 1 mA (line). The arrows designate the frequency below which the responses become significantly different.

sometimes also as low as at ca. 0.5 mHz). Notably, the two-mode behaviour was found to be independent of the direction of frequency sweep, that is, the impedance responses had the same main features, regardless whether we started the measurement at the highest or at the lowest frequency.

The results shown in Fig. 2a and b indicate that at least the high frequency part of measured spectra (recognized as being independent of the amplitude of excitation signal) could be a good candidate for an LTI response. To check this most rigorously, we performed several additional tests. First, it is worth noting that, in the region in which the material displays a linear behaviour, the response can be very well fitted using a simple equivalent circuit, typically consisting of no more than four elements (e.g., two resistors and two CPE elements). Moreover, as expected from Fig. 2a and b, the circuit element values have been found almost independent of the amplitude of excitation signal (e.g., upon variation of amplitude by 2 orders of magnitude, the variation of circuit elements is in the range of several percent, that is, in the range of experimental error).

A true test of the linearity of a system, however, relies on the analysis of higher harmonics of the response signal. Such a test is available in certain commercial equipments, such as in Solartron Frequency Response Analyzer (FRA 1250). Prior to using this option on the LiFePO$_4$ system, we checked it on a commercially available resistor and a diode—the former being a typical linear and the latter a typical nonlinear system. As expected, the response of resistor contained negligible second

and higher harmonics. On the contrary, the response of diode exhibited significant amplitudes of second (Fig. 3) and higher harmonics, in agreement with the known characteristics of this electronic device [12]. The results for the present system of interest, LiFePO$_4$, are shown in Table 1. It can be seen that at all frequencies tested, the amplitudes of the second and third harmonics are negligible in comparison to the amplitude of the first harmonic, which undoubtedly confirms that LiFePO$_4$ behaves linearly at these conditions.
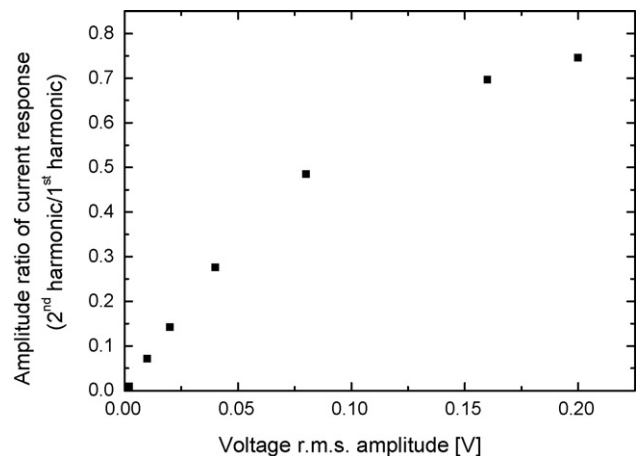

Fig. 3. Harmonic analysis of a diode ($E = -0.401$ V). At higher excitation amplitudes, the amplitude of second harmonic of the response signal becomes comparable to that of the first harmonic (the ratio approaches to 1).

Table 1
The values of three harmonics of excitation and response signal while measuring the impedance of $LiFePO_4$ in the middle of charge–discharge voltage plateau

Frequency (mHz)	Channel	Harmonic (mV)		
		1st	2nd	3rd
103.87	Excitation	10.041	0.000	0.000
	Response	1.80	0.00	0.00
10.387	Excitation	10.042	0.003	0.010
	Response	2.60	0.00	0.00
2.072	Excitation	10.041	–	0.001
	Response	3.20	0.00	–

Three frequencies within the linear region (see Fig. 2) were analyzed.

In the last test we additionally checked the regularity of the frequency domain measurement (impedance response) by comparing its main features to the corresponding time domain measurement. As mentioned before, the impedance measurement – in the part where it satisfies the condition of linearity – is dominated by a diffusion-like response: impedance is here a function of the square root of frequency. If such an impedance response is inverse-Fourier-transformed into time domain, then in the case of step excitation the response signal will exhibit the well-known square-root dependence on time.

Fig. 4 shows the square-root-of-time dependence of the voltage response upon galvanostatic step excitation of the $LiFePO_4$ cathode. Prior to galvanostatic excitation, the cell was equilibrated in the same way as in the case of impedance response measurements (24 h at OCV). There is a clear linear region extending up to several hundred seconds, which is in complete analogy with the $(i\omega)^{0.5}$ dependence of impedance observed at intermediate frequencies (from ca. 10 to 0.1 Hz or lower). The fact that the time domain measurement gives qualitatively the same result as the impedance response measurement, additionally rules out the possibility of artefacts in impedance measurements due to filtering or other equipment-specific artefacts.
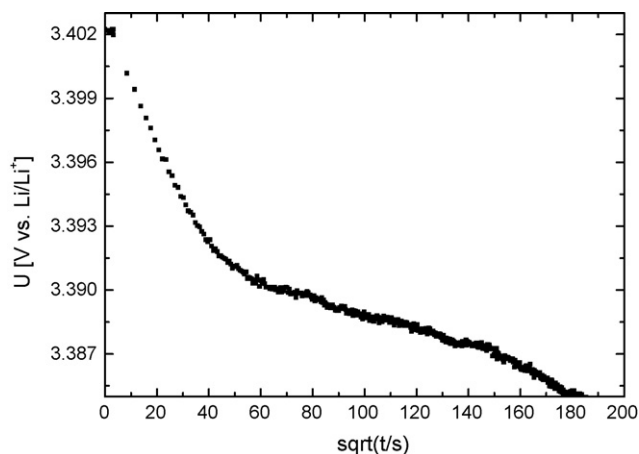

Fig. 4. Voltage response to a galvanostatic charge of $Li_{0.5}FePO_4$. The amplitude of current step was 0.85 mA g^{-1}.
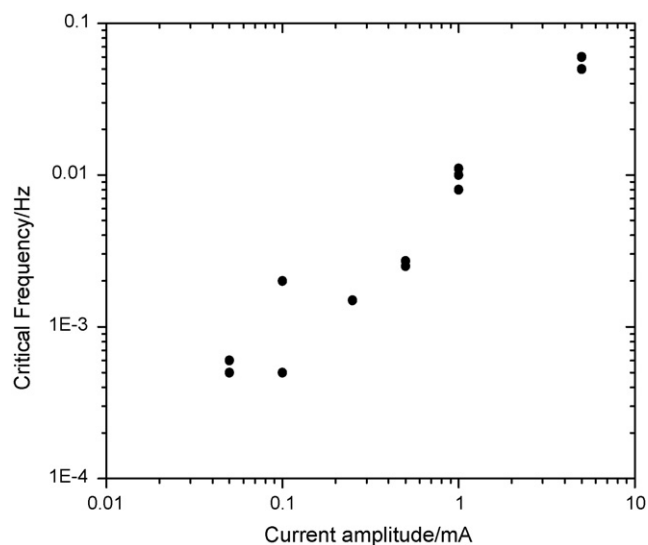

Fig. 5. Critical charge as a function of current excitation amplitude. The critical charge was determined by integrating the half-wave of excitation signal at critical frequency. The mass of $LiFePO_4$ in electrode was 7.5 mg.

Once the dual nature (LTI at high frequencies and non-LTI at low frequencies) of the impedance response of $LiFePO_4$ in region B (see Fig. 1) had been clearly confirmed, we wanted to identify more accurately the critical frequency (ν_c) that separates the two regimes. Analyzing a number of impedance spectra measured in a wide frequency range (10^6 to 5×10^{-5} Hz) and at different amplitudes of excitation signal (from 0.05 to 5 mA), we found that there existed no unique value of ν_c. Rather, ν_c seemed to increase quite uniformly with increasing amplitude of the excitation signal (Fig. 5). The physico-chemical background of this interesting phenomenon is still under investigation.

4. Conclusion

The typical impedance response measurement taken on the voltage plateau of $LiFePO_4$ charge–discharge curve may be divided into two regions: a region where the material displays a linear behaviour, which extends above a critical frequency that lies in the range from 0.5 to 100 mHz and a region that lies below this critical frequency where the material displays a non-linear behaviour. We proved by (i) measuring the dependence of impedance response of $Li_{0.5}FePO_4$ on the mode (voltage, current) and amplitude of excitation, (ii) analysis of higher harmonics of response signal, and (iii) comparison of impedance response with time-domain measurements, that the high frequency response (above 100 mHz) is linear and time invariant (LTI). The critical frequency at which the transition from LTI to non-LTI behaviour occurs, depends on the amplitude of current excitation signal.

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