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Determination of suitable parameters for Battery Analysis by Electrochemical Impedance Spectroscopy

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Abstract—Electrochemical Impedance Spectroscopy (EIS) is one of the most powerful tools for the study of batteries. The applied AC current, range of frequency sweep, points per decade represented, length of the pause time after a change in the state of charge (SOC) and length of the pause time after a change in the state useful results from EIS tests. A method to determine and optimize these parameters is presented in this paper. It is based on the limits imposed by the battery, the tests carried out, the instruments employed and the use of Kramers-Kronig relations. The method has been checked using two kinds of lithium batteries: a lithium iron phosphate (LFP) battery and a lithium cobalt oxide (LCO) battery.

Keywords— Lithium batteries, Electrochemical Impedance Spectroscopy (EIS)

1. Introduction

In recent years, Li batteries have been widely used [1] in different applications due to their high energy and power density, low self-discharge, low maintenance, variety of technologies available, long life, environmentally friendliness and low toxicity [2], [3].

Li-ion battery technology is accordingly considered for a wide range of applications such as renewables, automotive industry and mobile electronic devices [4], [5].

Electrochemical Impedance Spectroscopy (EIS) is one of the most useful techniques for characterizing and modeling batteries [6] as it can provide detailed information on the systems under non-destructive examination [7].

EIS allows the development of dynamic battery cell models whose elements can be allied to the physico-chemical processes that arise inside the battery [8],[9],[10]. EIS tests also allow the study of electrochemical mechanisms, reaction kinetics [11],[12],[13],[14], detection of localized corrosion [15], battery life performance [16], state of charge (SOC) [17], cathode [18],[19],[21],[22], [23] and anode [24], [25], [26], [27], [20], [28] materials in lithium batteries, the kinetics of lithium-ion intercalation [7], [29], factors responsible for the loss of capacity [11], lithium diffusion coefficients [8], factors responsible for overall impedance during Li-cycling [27] and parameters related to the transport of intercalation materials [30].

EIS tests can be carried out in potentiostatic or galvanostatic

mode. In potentiostatic mode, a small sinusoidal AC voltage is applied over a given range of frequency sweep to a battery and the resulting battery current is measured. In galvanostatic mode, a small sinusoidal AC current is applied over a given range of frequency sweep to a battery and the resulting battery voltage is measured [31], [32]. Potentiostatic mode is poorly suited for batteries due to their low impedance: a small error in the applied AC voltage, e.g. 1 mV [33], could produce an unexpected high current that could modify the battery SOC. However, as a galvanostat can easily control the applied current to an accuracy of a few milliamps, the battery voltage and SOC are usually unaffected when the galvanostat is connected to the battery [34]. Consequently, galvanostatic mode is recommended for batteries [34].

There are on line EIS techniques for batteries for on board use of a Battery Management System (BMS) operating on line in an electrical vehicle (EV). These techniques allow the onboard impedance to be obtained using techniques with suitable excitation, simultaneously including a number of frequencies, such as pseudo random binary sequences (PRBS). These types of techniques are more likely to generate noise and the impedance thus obtained has a greater error in high frequencies than when using classical EIS techniques. Other qualities of these techniques are that they are cheap and fast and that is possible to track the changes in impedance during the use of the EV to obtain on-board state of health (SOH) information [35]. However, the present study focuses on a laboratory EIS because we wish to obtain the impedance function of cells in a wave frequency range in the most robust and accurate way possible.

Nyquist plots, which plot the imaginary part of the impedance versus the real part, are one of the most useful plots to represent and analyze the results of EIS tests [36], [37]. Optimum Nyquist plots should be repeatable, not have noise and show five different sections, each one related to a particular process. From the highest to the lowest frequencies, see **Fig. 1**, Section 1 shows inductive behavior. Section 2 shows the ohmic resistance of the battery, which is determined by the intersection of the plot with the real axis. Section 3 is associated with the solid electrolyte interphase (SEI) on the graphite electrode. Section 4 represents the double layer capacitance (DL), the charge transfer (CT) resistance at the electrodes, and the surface film (SF) resistance on the cathode. Sometimes the lowest frequency region of Section 4 contains

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