Journal of Energy Storage 11 (2017) 76–85

Contents lists available at ScienceDirect

Journal of Energy Storage

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

Influence of high intensive dry mixing and calendering on relative electrode resistivity determined via an advanced two point approach

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ARTICLE INFO

Article history:
Received 7 October 2016
Received in revised form 1 February 2017
Available online 28 February 2017

Keywords:
Lithium-ion battery
Electrode resistivity
Resistivity measurement
Dry mixing
Calendering

ABSTRACT

In order to achieve a profound understanding of the production process of electrodes for lithium-ion batteries, methods to determine the (intermediate) product quality are a necessity. Therefore, a new, fast and easy to use two point method to determine the relative resistivity of dry electrodes has been established. The method is used to determine process-induced changes in the electrode's structure. A materials testing machine is used to ensure a homogeneous and constant mechanical stress during the analysis. By applying a direct current and measuring the voltage drop the electron transport characteristic along the whole electrode cross-section, taking all battery relevant resistances into account, can be determined. The result is an easy to compare relative resistivity value including coating resistance, contact resistance between coating and adhering current collector as well as the contact resistances between sample and probe. Process-induced changes are clearly visible in the results. The influence of the main testing parameters – contact stress and applied current – is determined. To cross-check the results, an established 'powder probe' method is used to confirm the relative resistivity changes caused by calendering. Slight calendering of $LiNiMnCoO_2$ cathodes leads to an increase in electrode resistivity as conductive pathways are broken by the applied shear forces. However, increasing the cathode density to 2.95 g/cm^3 decreases resistivity by one third compared to uncalendered electrodes by re-establishing and shortening electrical pathways. Furthermore, a relative resistivity of anodes produced with a high energy powder mixing step is measured and shows that applying too much stress to the carbon black leads to a loss in long range conductivity, resulting in electrodes with an increased resistivity of up to 50%.

1. Introduction

The pathways for electrons travelling lithium-ion battery cathodes have to be constituted by micro- and nanostructures of the conducting agents (e.g. carbon black), as the active material (AM) used in cathodes almost isolates. In negative electrodes, utilizing graphite as active material, the binder (B) decreases the conductivity inside the coating depending on the interaction and distribution of the carbon black (CB) particles. Additionally, graphite serves as an electron conductor itself, thus the level of complexity for electron transport processes increases. In order to gain process control and to improve battery performance it is necessary to gather more information about the formed structures inside the composite electrode. Therefore, resistivity data is important to compare resulting electron transport characteristics, monitor intermediate product quality (e.g. homogenous component distribution [1]) as well as to gain process control and process stability. The advanced two point method (ATPM) used in this work is able to support battery manufacturing, by providing intermediate product information way before the cell is assembled and e.g. electrochemical impedance spectroscopy can be applied. Furthermore, the obtained results present first insight in correlation between production process, electrode structure and electrode quality.

In general an electrode consists of a current collector which is coated from both sides with a particulate coating, containing a polymeric binder to provide proper adhesion [2]. This definition is

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http://dx.doi.org/10.1016/j.est.2017.02.001
2352-152X/

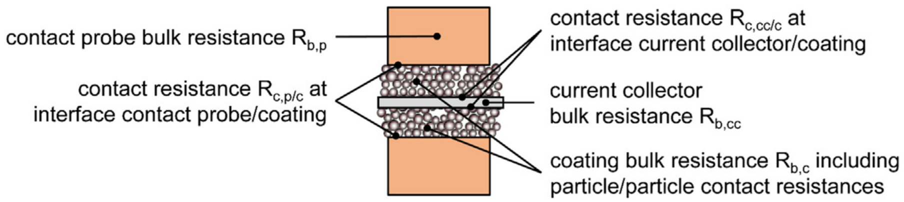

Fig. 1. Relevant resistances of a double-side coated electrode at any two point probe measurement.

used throughout the whole text: electrode = coating + current collector. Fig. 1 shows a two-side coated electrode labeled with all current transport relevant resistances of an electrode during any two point probe measurement method. 'Contact probe' is used as expression for all possible contact mechanisms (e.g. powder [3], metal probe or stamp, liquid), each differing in value and properties.

The resulting bulk electrode resistance $R_{b,electrode}$ is given by the sum of all relevant resistances (see Eq. (1)). Additionally, $R_{b,c}$ includes all resistances inside the coating which are mainly particle/particle contact resistances and particle bulk resistances.

$$R_{\mathrm{b,electrode}} = 2 * R_{\mathrm{b,p}} + 2 * R_{\mathrm{c,p/c}} + 2 * R_{\mathrm{b,c}} + 2 * R_{\mathrm{c,cc/c}} + R_{\mathrm{b,cc}} \qquad (1)$$

As copper (5.96×10^7 S/m), aluminum (3.5×10^7 S/m) and all probe materials are highly conductive, the bulk resistivity of the current collector and the probes play a minor part.

In literature, the four point probe method is often used to determine the electrical resistance of electrodes for battery application [4–8]. Historically most four point probe methods have been especially designed for thin coatings on non-conductive substrates or considerably infinite thick samples [9–11]. Model coating layers on non-conductive substrates are used to avoid a shunting path towards the substrate and to measure battery electrodes accurately [7]. Even if shunting paths can be avoided (e.g. by adjusting probe distance [12]), the resulting values still only describe the resistivity of the coating, as the direction of current transfer is parallel to the coating, neglecting the contact resistance at the interface substrate to coating layer. The reason why the four point probe method is preferred to determine absolute values, even though pressed pellets [13,14] or model coatings have to be used, is that four point probe avoids contact resistance $R_{c,p/c}$ between the probe and the specimen. Thus, it is applicable to determine absolute electrical resistances of the coating, on the expense of direct transferability to battery electrodes. Furthermore, coating layers in battery applications are considerably thick (60–150 μm). Only a section of the coating layer contributes to the resistivity if four point probe is used, neglecting unintentionally induced or desired structure gradients [15,16] of the coating.

An easy to use, advanced two point probe method (ATPM) to determine the process-induced resistivity changes of an electrode (current collector + coating) is presented in this work. No sample preparation either than punching a circular area is needed. Even though the method cannot exclude contact resistance at the interface probe/coating $R_{c,p/c}$, or quantify the probe/current collector $R_{c,p/cc}$ separately, it depicts the real electron pathways in battery electrodes. The pathways of electrons are directed in z-direction from particulate surface to current collector or vice versa. This direction is ensured by applying the current on top of the electrode and providing the other electrical contact on the bottom (see Fig. 1). Using double-side coated electrodes the contact resistance at the interface current collector/coating $R_{c,cc/c}$ and the bulk resistance of the coating $R_{b,c}$ is measured twice (see Eq. (1)). However in this work single-side coated electrodes are investigated. According to this, electrons flow over the entire application-relevant height of the electrode, thus, passing through any limiting structure. This is equivalent to electron movement in any electrode during cycling in a lithium-ion battery.

Besides the disadvantage of inevitable parasitic contact resistance at the probe/electrode interface which hinders ATPM from measuring absolute values, it shows three major advantages:

- Close to the application electron transport
- Result is a single value, which contains all battery relevant resistances, which can be influenced by electrode production. Summing up volume resistance of current collector and coating (containing all contact resistances amongst the particles) and contact resistance at the interface current collector/coating.
- Easy to set up and use in any force controlling device (e.g. materials testing machine) or even within the production line

Particle interactions with the current collector, particle-particle contacts inside the coating (e.g. CB-AM, AM-AM, CB-CB) and particle binder composites are influenced by formulation strategy [17–19], mixing and dispersing [20–23], drying [1,24,25] and calendering [7,26–28]. Thus changes in contact resistance at the coating/current collector interface as well as the coating bulk resistance are strongly dependent on the production process (process-structure relationship) and have to be determined as an overall electrode resistivity.

In order to confirm that a process-depended change in electrode resistivity is detectable by ATPM, even though the contact resistance between coating and probe is included, a second method which reduces this contact resistance is used to verify the results [3]. Furthermore, Indrikova et al. show that two point probe methods are capable of measuring the relative electrode resistivity [29].

2. Material and methods

2.1. Materials and electrode production

The single-side coated electrodes were produced using a distributive dry mixing process (in a rotary drum mixer) for dry powder homogenization at a tip speed of 0.3 m/s for 30 min. The dispersing is done at 9 m/s tip speed for 60 min in a cooled, rotating disc dissolver (Dispermat CA60, VMA Getzman GmbH). A continuous coater/dryer combination (Labco, Kroenert GmbH & Co KG) with a production speed of 2 m/min is used to coat the suspension on the current collector and to evaporate the solvent using a linear temperature profile form 80–120 °C along the dryer length of 6 m. As active materials $LiFePO_4$ (LFP: LFP-P2, Clariant), $LiNiMnCoO_2$ (NMC1: NMC 3100, Toda and NMC2: NMC HED111, BASF SE) and two different graphites (Gr1: MAGD20, Hitachi and Gr2: MCMB10-28, Osaka Gas) are used to prepare suspensions based on N-Methyl-2-Pyrrolidone (NMP) as a solvent. Polyvinylidenedifluoride (PVDF) serves as a binder (B, Solef, Solvay GmbH), while carbon black (CB, Super P-Li, Timcal) and if stated a conductive graphite (CGr SFG6L, Imerys Graphite & Carbon SA) are utilized as conductive agents. All recipes and the solids content can