Plasma Source and Process to Minimize Electrical Contact Resistance of Metal Surfaces and Compounds

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Abstract: Most metals develop surface layers of their oxides after production or storage under ambient conditions. Metal oxides often exhibit insulating electrical properties. This may cause disadvantages in further processing or application. The article describes results of a plasma technology incorporating the use of fine particles of carbon. The goal is the improvement of the electrical conductivity of aluminum surfaces and carbon containing composites attached to aluminum.

Keywords: Lithium cell, battery, aluminum, carbon, capacitor, electrical resistance

1. Introduction

Aluminum foil is commonly used in various energy storage systems. In the case of lithium-ion cells specific composite materials consisting for example of lithium-cobalt- or lithium-nickel-dioxide are being attached to aluminum foil that works as current collector. The resulting laminate constitutes the cell's cathode [1]. Another example for the usage of aluminum as collector is an ultracapacitor or double layer capacitor, respectively [2].

Aluminum foil is a fairly cheap material with a low specific weight and good electrochemical stability in lithium ion cells. This results from the fact that aluminum instantly develops a protecting surface layer of its oxide (alumina film) plus hydroxides after production or storage under oxygen or water containing conditions. A grave disadvantage is, on the other hand, the extremely high electrical resistivity (10^{12} – 10^{15} Ωcm) and the dielectric character of native alumina films that cause intolerable electrical losses between collector foil and the composite material [3].

A number of methods have been patented in order to tackle problems that are related to contact resistances of aluminum surfaces or resistances that occur in the interface of the collector and the composite material [4, 5, 6]. In electrode fabrication chemical treatments (e.g. surface etching) of aluminum foil along with the application of so called 'conductive primer coatings' is state of the art [7]. Typical coatings are solvent-based dispersions of graphite in a thermoset binder [8].

Figure 1 depicts a cathode that consists of the collector foil (centre) which is covered with a conductive primer coating (black interfacial layer with a thickness of about 2 µm) on both sides. The electrochemical active composite is a lithium-cobalt-nickel-oxide (round particles). The composite's matrix comprises a binding media which is supplemented with conductive carbon (5 wt. % to 10 wt. %).

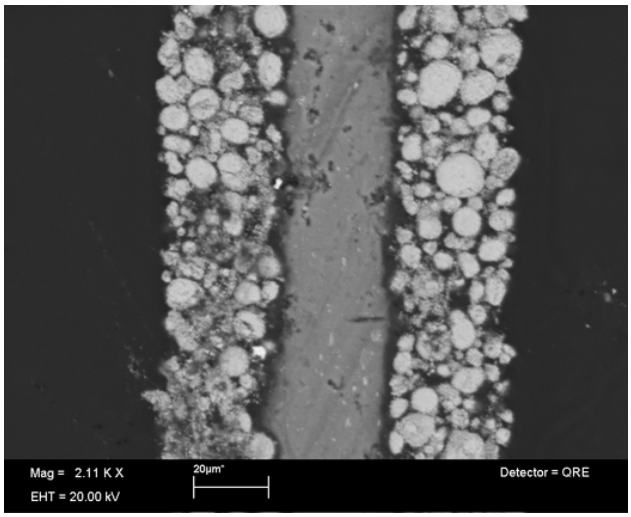

Figure 1: SEM image of a cathode from a lithium-ion cell

Apparently, the application of primer coatings is an expensive process. The principal goal of our approach is the development of a plasma based technology that facilitates the substitution of the primer treatment by a plasma process. This article highlights first activities in promoting a reduced contact resistance of an aluminum surface as well as reduced electrical resistance of the electrode laminate.

2. Experimental

The experimental set-up consists of a carbon generator (PALAS GFG 1000), a high voltage AC power supply, a glass discharge tube and the substrate mounted on an x-y-z manipulator table (**figure 2**).

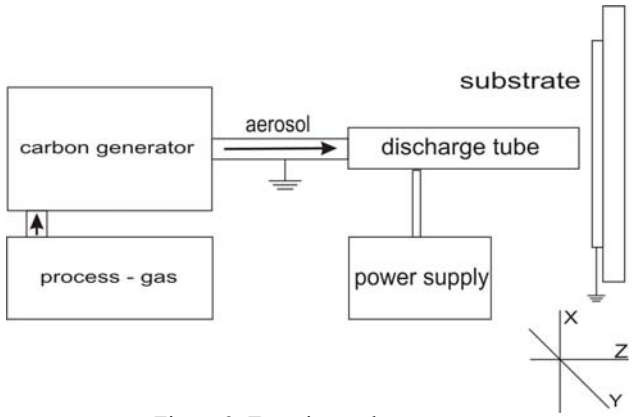

Figure 2: Experimental setup

With the carbon generator a flashover between two graphite electrodes is produced by high voltage. Graphite evaporates in a gas mixture of Argon (95%) and H_2 (5%). During further transport in the gas flow it agglomerates. The particle size-distribution of these agglomerates depends on the spark frequency, the gas flow and the pressure. The distribution ranges between 20 nm and 300 nm. The carbon particle mass-flow can be regulated from 0.07 mg/h to 6 mg/h [9].

The power supply produces series of decreasing sine pulse packages with peak pulse voltages of approximately 25 kV at a repetition rate of about 8 kHz. The carbon aerosol is introduced into the discharge tube. As the plasma is being ignited, micro-discharges (plasma filaments) develop in the jet like effluent. They are directed towards the surface of the grounded substrate. The plasma can be generated in the gas mixture without carbon supplemented as well.

Aluminum foil (99.8 %, TOYO Aluminum K.K.) with a thickness of about 25 µm was cut and cleaned in a ultrasonic bath (1 min. in acetone). Electrode laminate was delivered by a battery manufacturer.

Morphological and chemical properties of the two types of specimens were investigated using light microscopy, Atomic Force Microscopy (AFM) and X-ray Photoelectron Spectroscopy (XPS). In order to investigate the electrical characteristics voltage measurements were performed. The measuring setup is depicted in **figure 3**. As indicated in this figure, a linearly rising voltage (denoted by U_{ramp}) is supplied to the series connection of the substrate and a measuring shunt. The ramp signal and the potential drop of the shunt are captured by an oscilloscope.

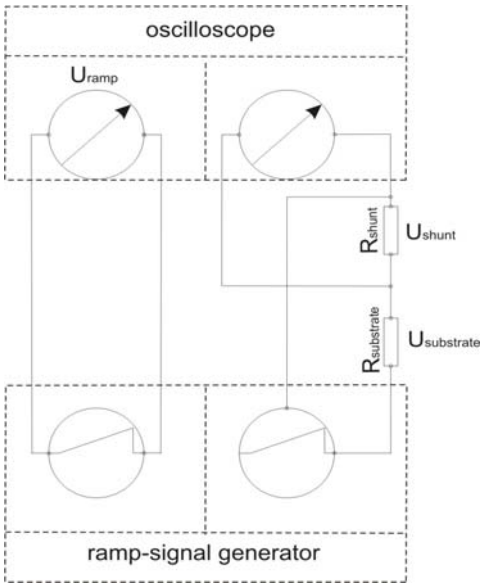

Figure 3: Measuring setup

The electrical resistance of the substrate can be calculated in the following manner:

$$R_{substrate} = R_{shunt} \cdot \frac{U_{ramp} - U_{shunt}}{U_{shunt}} \qquad (1)$$

$R_{substrate}$ denotes the resistance of the substrate, R_{shunt} is the resistance and U_{shunt} the potential drop of the shunt. As the enumerator in (1) equals the potential drop of the substrate ($U_{substrate}$), voltage-voltage curves can be plotted that visualize electrical characteristics. In order to contact the surface of the aluminum foil sensitively, a small drop of mercury was used as contact media.

3. Results and discussion

3.1 Treatment of aluminum foil

The plasma treatment of aluminum foil operating the carbon generator with a high spark frequency results in a carbon deposition on the surface as can be seen in **figure 4**. The material appears to be connected to the surface and strongly adheres to it since particles did not detach in the course of cleaning attempts.

An electrical characteristic of untreated and treated aluminum foil is given in **figure 5** and in **figure 6.** Each diagram contains datasets of ten single measurements in distinct areas. The potential drop of the substrate is de-

picted as a function of U_{ramp}. R_{shunt} was 1 kΩ in both cases.

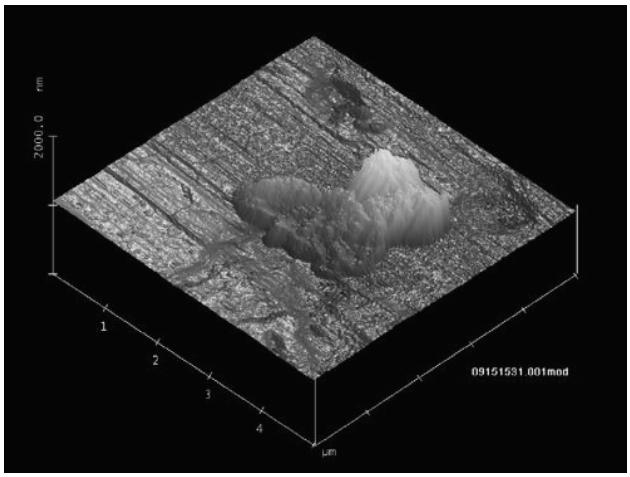

Figure 4: AFM image of a deposited carbon particle

All curves in **figure 5** show a gradient that is almost one until a sharp decline at about 3 V occurs. This phenomenon can be regarded as a dielectric breakdown of the native alumina film. It is reported that an electric field strength in the range of 0.55 V/nm to 1 V/nm induces a dielectric breakdown in thin alumina films on an aluminum substrate [10, 11]. According to XPS measurements applying a non-monochromatic X-ray source (Specs RQ20/38C) and a hemispherical analyzer (VSW HA100) under ultra high vacuum conditions, the aluminum foil is covered with a 4.45 nm thick layer of Al_2O_3. Details on the setup and the calculation procedure can be found in [12].

The detected value of 3 V for the dielectric breakdown is thus in good agreement with the cited investigations and the XPS results.

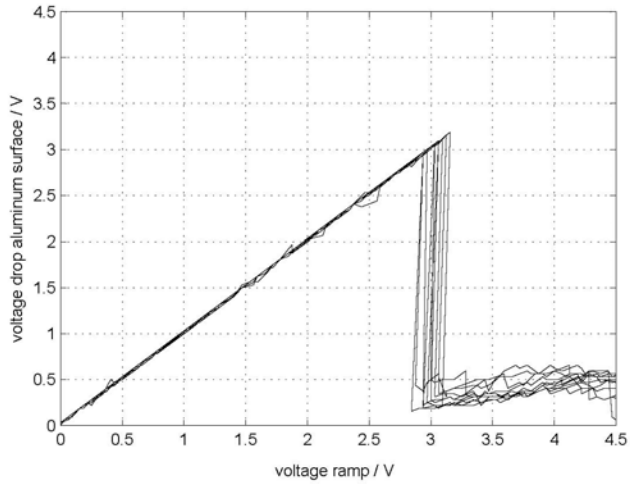

Figure 5: Untreated aluminum foil

As can be seen in **figure 6** the plasma treatment (8 cycles, carbon particle mass flow 6 = mg/h) leads to significantly reduced breakdown voltages.

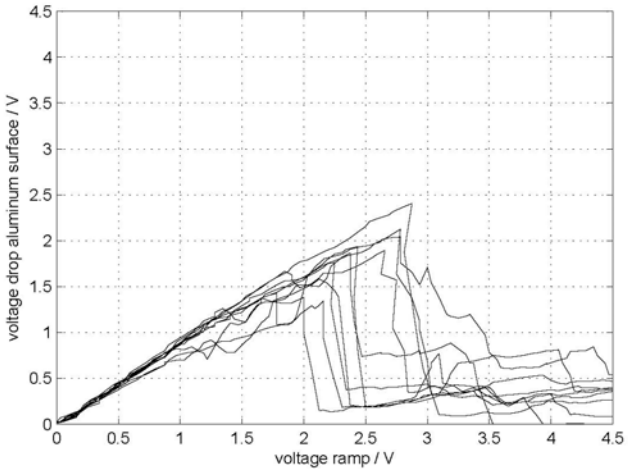

Figure 6: Plasma-treated aluminum foil

3.2 Treatment of aluminum foil plus active composite

The second approach targeted improvements by the treatment of aluminum foil that did not get a preliminary primer coating but was directly covered with active composite. Treatment was carried out with the carbon generator disabled. By means of current measurements during the plasma discharge (Pearson Current Monitor 10 A / 1 V mounted around the ground wire) it was found that a current flow up to 70 A takes place.

In **figure 7** a comparison of the contact resistance of an untreated vs. a plasma treated (1 cycle) specimen is given. The resistance decreases from roughly 100 Ω to approximately 30 Ω. The latter value is similar to the volume resistances of specimens that had been prepared with a conductive primer coating.

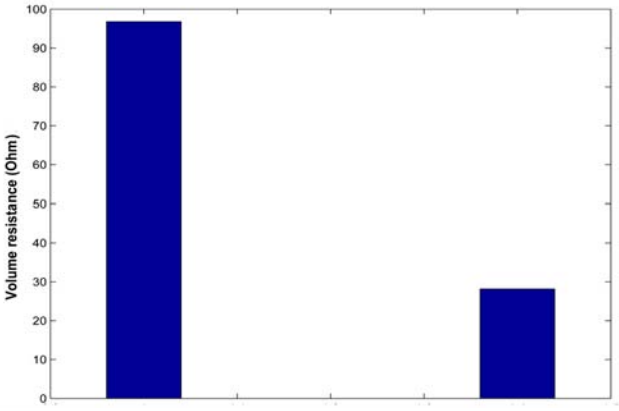

Figure 7: Contact resistances of untreated (left) and plasma – treated specimens (right)

Figure 8 shows XPS spectra of the surface of untreated and treated electrode laminate. The photoelectron count rate is plotted versus the electron binding energy with respect to the Fermi level. One can identify photoelectrons emitted from distinct atomic orbitals (for example F 1s) as well as electrons arising from Auger transitions (for example F(KLL)). The spectra reveal changes in the composition of the surface of the electrode laminate during plasma treatment. While the content of oxygen and lithium increases, a decrease of carbon and fluorine takes place. Due to the low information depth of XPS (about 10 nm), neither cobalt nor nickel can be detected.

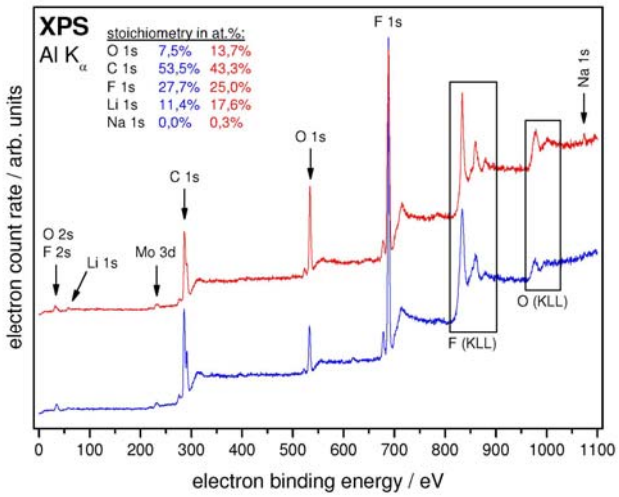

Figure 8: XPS spectra of untreated (bottom curve) and plasma treated active composite (top curve)

4. Conclusion

The plasma treatment of aluminum foil using an aerosol of micro-sized carbon aggregates in a mixture of Argon and H_2 permits a local deposition of carbon on the aluminum surface [13]. So far it was not possible to deposit and adhere carbon in high rates. The limiting factor is probably an insufficient mass-flow of the carbon generator. Nonetheless an improvement of electrical conductivity could be verified.

The plasma treatment of the chosen electrode laminate leads to a significant improvement of the volume conductivity. Further investigations on other electrode composites will have to be carried out in order to evaluate the results.

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[13] Patent protection is aspired and in course of the application procedure: DE 10 2009 002 320.