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## ABSTRACT

Characterization method for active layers of electrochemical and gas sensor electrodes, using scanning electron microscopy (SEM) is presented. In order to achieve maximum sensitivity and selectivity of the sensor, it is necessary to obtain precise knowledge of electrode's surface. Characterization was made using FEI Magellan SEM equipped with TLD secondary electron (SE) and CBS back-scattered electron (BSE) detectors, Energy-dispersive X-ray spectroscopy (EDS) and beam deceleration system. At lower energies, the SEM offers several advantages, the most important among them being: an increased material contrast, high ratio SE, BSE signal and noise, a smaller interaction volume and elimination of charging effects.

## INTRODUCTION

Electron microscopy (EM) is considered to be a suitable tool to characterize homogeneity and material composition of the CNTs based surface layer. Reflected electrons are commonly used for imaging of bulk specimens: **low energy secondary electrons** (0–50 eV) provide information about topography, whereas **high energy backscattered electrons** (> 50 eV) provide information about the material composition of the structure [7]. At electron energies for conventional SEM, the impinging electrons are elastically scattered by atom cores making the scattering rate proportional to the atomic number of the target. The incident electrons are scattered into an interaction volume of a diameter of tens of micrometers [8]. There is a special part of EM called LVSEM (Low Voltage SEM) operating usually with energies **lower than 5 keV**. Among the most significant advantages, the most important is that the beam interaction volume **diminishes rapidly**, yielding more surface sensitive information [8]. Additionally, it is possible to work with **uncoated samples** without significant charging originating from nonconductive particles present on the specimen. It is possible to **suppress charging** when working on particular energy which is called the "critical energy" and which differs for each material [7]. Therefore, this technique **allows performing additional element analysis** (Energy-dispersive X-ray Spectroscopy or Auger Spectroscopy) on the same specimen.

## ELECTRODE DESCRIPTION

Electrode substrates were fabricated on a 0.65 mm thick alumina using standard screen-printing technology. The contact layer was made of **platinum paste** ESL 5545 and the protective layer from ESL 4917

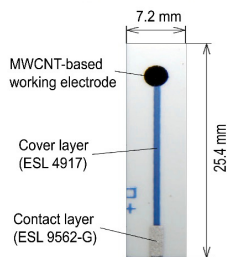


Fig. 1: Working electrode configuration

MWCNTs active layers were fabricated using **spray-coating method**. For this purpose, MWCNTs were dispersed in N,N-dimethylformamide (DMF) and then spray-coated over stencil template. The diameter of round electrode/active layer was 3 mm.

## ELECTRODE CHARACTERIZATION

First task dealt with the characterization of the **base platinum layer** on which the MWCNTs are sprayed. In order to obtain surface image, it was necessary to reduce the interaction volume of the impinging electrons. This was achieved by **reducing the power of the primary electron beam** down to 5 keV, which increased the number of signal electrons and reduced the **charging effect**.

However, due to the necessity of characterization of **uncoated samples**, several problems connected with specimen charging occurred. For this reason, a **custom sampling method** based on a very short dwell time (1 μs) and line integration (30x) has been incorporated. This led to a significant lowering of the charging effect that originates from the non-conductive particles. Another problem was connected to the CBS (BSE) detector that attracted not only the BSE but also the SE. This has been solved by using of a **particular segment of the multi-segment CBS detector** that allowed separating the BSE and SE in order to obtain purely material contrast.

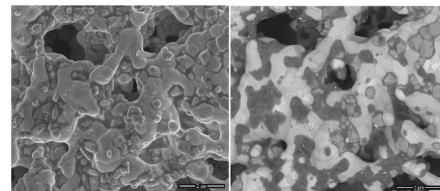


Fig. 2: Pt layer surface: a) SE (TLD detector), b) BSE (CBS detector) E = 5 keV, magnification: 10.000x

In the Fig. 2.a. it can be seen that the surface is more or less compact in order to create a **stable base** for the MWCNT film. However, when using the secondary electrons the grains can be seen very well, but it is **uneasy to distinguish** platinum grains among other grains that are present on the surface. For this reason, BSE image was obtained, as it is illustrated in Fig. 2.b. It can be seen that there are **various contrasts** and shapes belonging to several materials, where one material prevails. Possibilities of their origin will be discussed further in the text. From the backscattered electrons image, it can be seen that there is a **direct proportion** between image contrast and material conductivity. The most contrasting parts of the image are the non-conductive particles, whereas the dark parts are the residuals of additives.

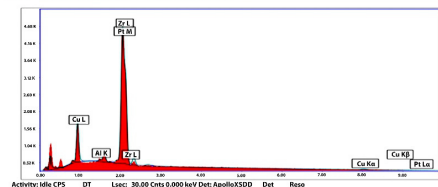


Fig. 3: Energy-dispersive X-ray spectroscopy of the Pt ink surface

From the Fig. 2.b., it can be seen that there are various elements present on the surface according to the **different contrast and reflectivity** (materials with higher atomic weight exhibit more contrast). Therefore, the results achieved by the SE and BSE are additionally supplemented by **EDS analysis** (Fig. 3). There, it can be seen that the Pt peak is prevailing, however, there are other materials present: the Cu peak originates from the specimen holder, the Al peak originates from the Al<sub>2</sub>O<sub>3</sub> electrode substrate and the origin of the Zr peak is still not yet fully clear and has to be verified by another analytical method.

Using the same EM configuration, the previously discussed Pt electrode covered by MWCNTs was investigated, as it is illustrated in Fig. 4. Information provided by SE proves that the surface is covered by the MWCNTs nearly uniformly. The image also shows that the clots of nanotubes are distributed not only on the Pt electrode, but also in the **interstitials**.

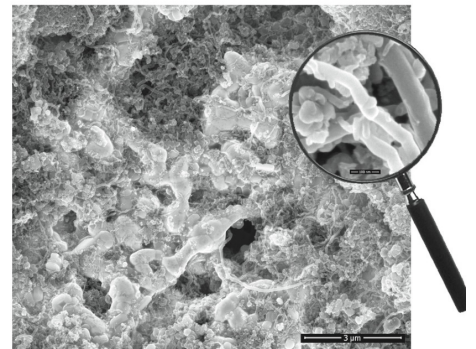


Fig. 4: MWCNTs-coated (3 ml sprayed) Pt layer surface (secondary electrons), TLD detector, E = 5 keV, magnification: 8.000x

Information brought from the surface by the CBS (BSE) detectors is illustrated in Fig. 5. It can be seen that the BSE neglect MWCNT clots in the interstitials **due to their higher energy**, however, they bring interesting information about the subsurface, revealing the **presence of the contaminant particles** that are hidden under the nanotubes.

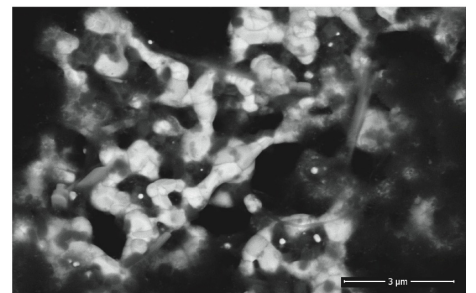


Fig. 5: MWCNTs-coated (3 ml sprayed) Pt layer surface (backscattered electrons), CBS detector, E = 5 keV, magnification: 8.000x

## CONCLUSION

A function electrode based on MWCNTs active layer has been analyzed by the SEM at **low energies**. It has been shown that various detectors bring different information about the surface. SE detector brings **surface information** about MWCNTs distribution in contrast to BSE detector which brings information about **material contrast**. Information brought by both detectors can be very helpful for electrode **surface characterization** and may be correlated to the electrochemical characteristics of the sensor provided by the **voltammetry measurements**.

## ACKNOWLEDGMENTS:

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