



Short communication

Application of electrochemical impedance spectroscopy to monitoring discharging process of nickel/metal hydride battery

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H I G H L I G H T S

- Impedance-oriented diagnostics of NiMH cells was applied.
- At the same time, changes impedance of cells components was obtained.
- The cell, where state are determined by the positive, negative or both electrodes.
- Dual-electrode measurements don't reflect the actual condition of the tested battery.

A R T I C L E I N F O

Article history:

Received 11 February 2013

Received in revised form

4 April 2013

Accepted 9 April 2013

Available online 19 April 2013

Keywords:

Electrochemical impedance spectroscopy

Nickel/metal hydride battery

Discharge

Diagnostic

A B S T R A C T

This paper presents the possibility of applying impedance analysis to cell diagnostics. In order to obtain characteristic curves of both electrodes of a NiMH battery simultaneously, a reference electrode was added into the circuit. The authors analysed the cell under three cases, i.e. when its properties are determined only by the state of the positive electrode, only by the state of the negative electrode, or when both electrodes determine operation of the cell to the same extent. Impedance characteristic curves of the entire cell in the function of variable state of charge do not allow for a conclusion as to which electrode determines cell capacity. This is not possible until an analysis of impedance graphs is carried out for each electrode. In view of the obtained results equivalent circuits for the positive electrode, the negative electrode, and the entire cell were selected. Further, a correlation between charge transfer resistance, calculated for the entire cell, and the values obtained for the positive electrode, as well as the negative one, is presented.

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1. Introduction

The demand for power sources in the form of rechargeable batteries is growing year by year, and this is attributable mainly to the continuous development of mobile electronic equipment. Therefore, there are stricter requirements specified for such cells as their higher and higher capacity, extended lifetime, and most importantly high reliability, are expected. At the same time, the smallest possible weight and size of such cells are required. Generally, such features are complied with by NiMH batteries, i.e. cells using hydrogen storage alloy as a negative electrode and nickel hydroxide as a positive electrode [1–3].

R&D projects devoted to the NiMH batteries apply charge/discharge characteristics, capacity change analyses, cycle life, cyclic

voltammetry studies and electrochemical impedance spectroscopy (EIS) measurements [4–8]. For the purpose of the analysis, the EIS method is applied most frequently [9–12]. It enjoys its popularity from being associated with the speed and non-destructive nature of the measurement, whereas obtained results allow for analysing mechanisms and kinetics of processes which take place in the circuit being investigated. In the case of testing impedance of NiMH batteries, measurements include a dual-electrode circuit where total impedance of the positive electrode, the negative electrode, the separator, and electrolyte is to be determined. Obtained impedance characteristic curves are conditioned by the state of such a cell, and thus, amongst other things, they can be employed in assessing their state of charge (SOC) [13,14]. Such as dual-electrode measurement allows for analysing results just by using simplified equivalent circuit diagrams, in which the components, apart from electrolyte resistance, cannot be associated with any specific electrode processes [15–17]. Therefore, they cannot be applied to precise diagnostics; it is not possible to verify which element limits the

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operation, properties of which one deviate from the rest, and as a result, which one affects the behaviour of the entire cell. The degree of cell consumption is not always associated with even degradation of electrodes, as it may also be caused as a consequence of damage or degradation of one of them. In order to obtain impedance changes which occur across individual electrodes in the NiMH battery it is necessary to apply an additional reference electrode. Such an approach, recently presented by the authors, allows not only for obtaining impedance values of individual elements, but also for tracking changes during the operation of an electrochemical cell [18]. Hence it becomes possible to apply the impedance method for actual diagnostics of the NiMH batteries, which is presented in this paper by means of a discharging process example.

2. Experimental

2.1. Model NiMH cell

The scheme of the investigated model of Ni/MH cell is presented in Fig. 1. Negative electrode weighs 0.125 g and consists of 90 wt.% of AB₅-type hydrogen-absorbing alloy powder of the formula LaMmNi_{3.55}Al_{0.3}Mn_{0.4}Co_{0.75} (<75 µm grain size) and 10 wt.% nickel carbonyl powder. The entire was pressed on nickel foam. The positive electrode weighs 0.145 g and consists of 88 wt.% of spherical β-Ni(OH)₂ powder as an active material, 2 wt.% metallic cobalt powder, 3 wt.% calcium oxide and 7 wt.% various carbon materials to improve the electrochemical properties. Positive electrode, the same as negative electrode was pressed on nickel foam. Firstly the electrodes were chemically and electrochemically activated. Therefore, the MH electrode was put into a boiling solution of 6 M KOH for 1 h period. Positive electrode was put into solution of 6 M KOH at room temperature for 24 h period. The next step was three times charging electrodes of current equal 5 mA to the first signal of gas evolution and therefore discharged current. Based on the third charge cycle was determination of the capacity of both electrodes, was similar, approx. 25 mAh.

The next step in making a model of NiMH cell was to put the electrodes into the polypropylene separator sheet and compressed

by Plexiglas casing. The Hg/HgO was used as a reference electrode. The electrolyte was 6 M KOH, the measurements were performed at room temperature. The process of discharging the model cell, as well as separate charging of individual cell electrodes with the use of an additional auxiliary electrode, was carried out at a dc current of 10 mA.

2.2. Electrochemical impedance

For the impedance measurements, multi-sinusoidal current excitation at a frequency ranging from 4.5 kHz to 30 mHz (170 mHz), generated by a PXI-4461 card, was applied. The amplitude and phase shift of the components were selected so that voltage amplitude of ac response did not exceed 25 mV_{pp} (peak to peak) during the measurement. The signal was input into Autolab 302N where it was added with the dc current signal, and then applied to the cell in question. During all measurements, a separate PXI-4462 card was used to record voltage signals, i.e. between cell electrodes, the positive and the reference electrode, and between the negative and reference electrodes as well. Such an approach allowed for obtaining the impedance of the entire cell as well as for every electrode separately. For analysing the results, the short-time Fourier transform (STFT) was applied, which allowed for obtaining impedance changes in the function of time, and as a result, in the function of deep of discharge (DOD). In this manner, any possible non-stationary influence was limited and a characteristic curve of any DOD was obtained within one measurement. This method has been discussed in detail by Slepski et al. in Ref. [19].

3. Results

In order to demonstrate how the impedance method can be useful as a tool for actual diagnostics of cells, along with others as in the case of NiMH, some experiments were carried out. In the first one, cell capacity depends evenly on the positive electrode and the negative one as well. In the second experiment, operation of the cell is determined by the state of the positive electrode, whereas the tested cell capacity in the third experiment is determined by the state of the negative electrode.

In the first experiment, the positive electrode was charged to the same extent as the negative one. Both electrodes were charged for 2.5 h. The impedance characteristic curve of the entire cell with relation to the state of charge is presented in Fig. 2a.

Fig. 2a shows a gradual increase in impedance for the highest DOD values which indicates that the cell was discharged. At the same time, impedance characteristic curves of individual electrodes during discharging were obtained. Fig. 2b presents an increase in positive electrode impedance occurring towards the end of discharging process. As shown in Fig. 2c, a similar dependence was revealed for the negative electrode. This means that the condition of the negative electrode and the positive one exert even influence on the capacity of the cell in question.

Then, two experiments reveal the cell condition where cell capacity depends on the condition of just one of the two electrodes. Being prepared for the second experiment, the positive electrode was charged for 1.25 h, whereas the negative electrode for 2.5 h.

An impedance characteristic curve of the tested cell with relation to the state of charge is presented in Fig. 3a. The presented diagram is strikingly similar to the one presented earlier in Fig. 2a. However, as has been mentioned, during the second experiment prior to discharging the cell, charge equal to a half of the nominal value was applied to the positive electrode. The impedance graphs shown in Fig. 3b, c represent impedance characteristic curves of the positive and negative electrodes as obtained within the same discharge cycle.

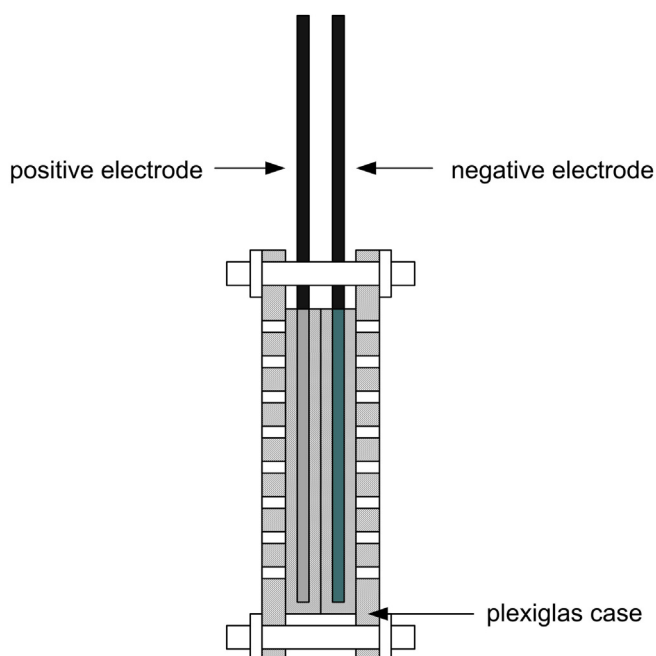


Fig. 1. The scheme of the experimental secondary cell.

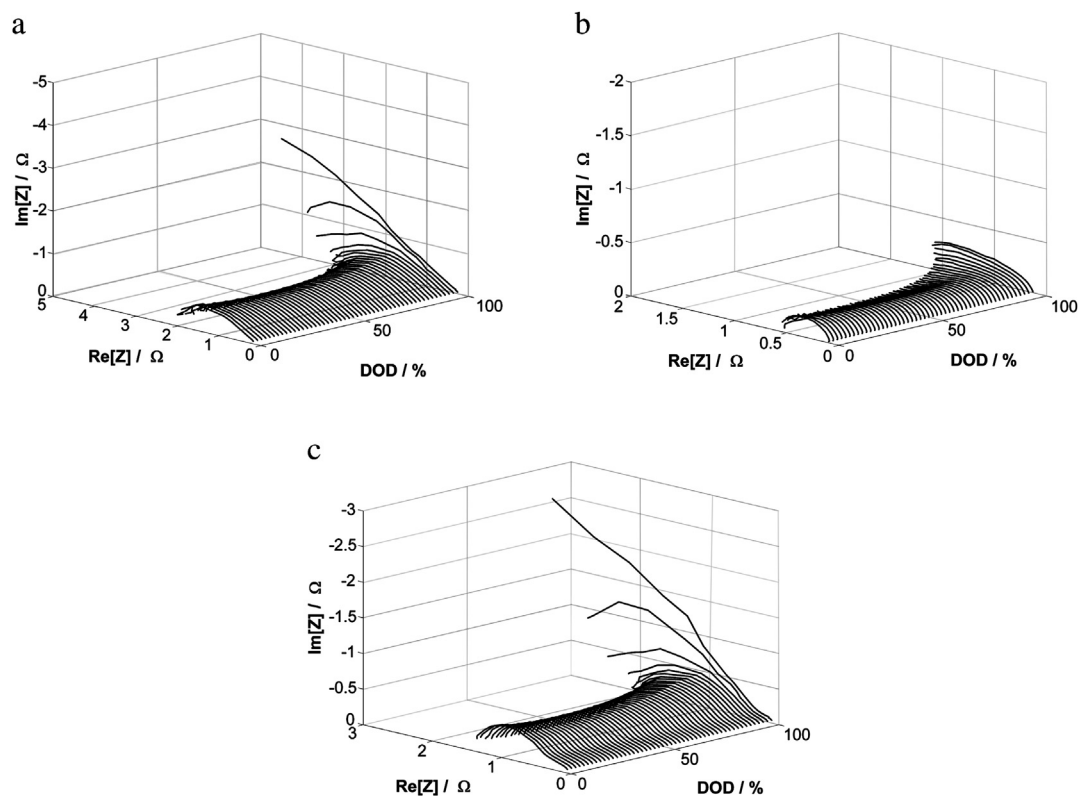


Fig. 2. a. An impedance characteristic curve of the entire cell whose capacity depends evenly on two electrodes in the function of DOD. b. An impedance characteristic curve of the positive electrode of the cell whose capacity depends evenly on two electrodes in the function of DOD. c. An impedance characteristic curve of the negative electrode of the cell whose capacity depends evenly on two electrodes in the function of DOD.

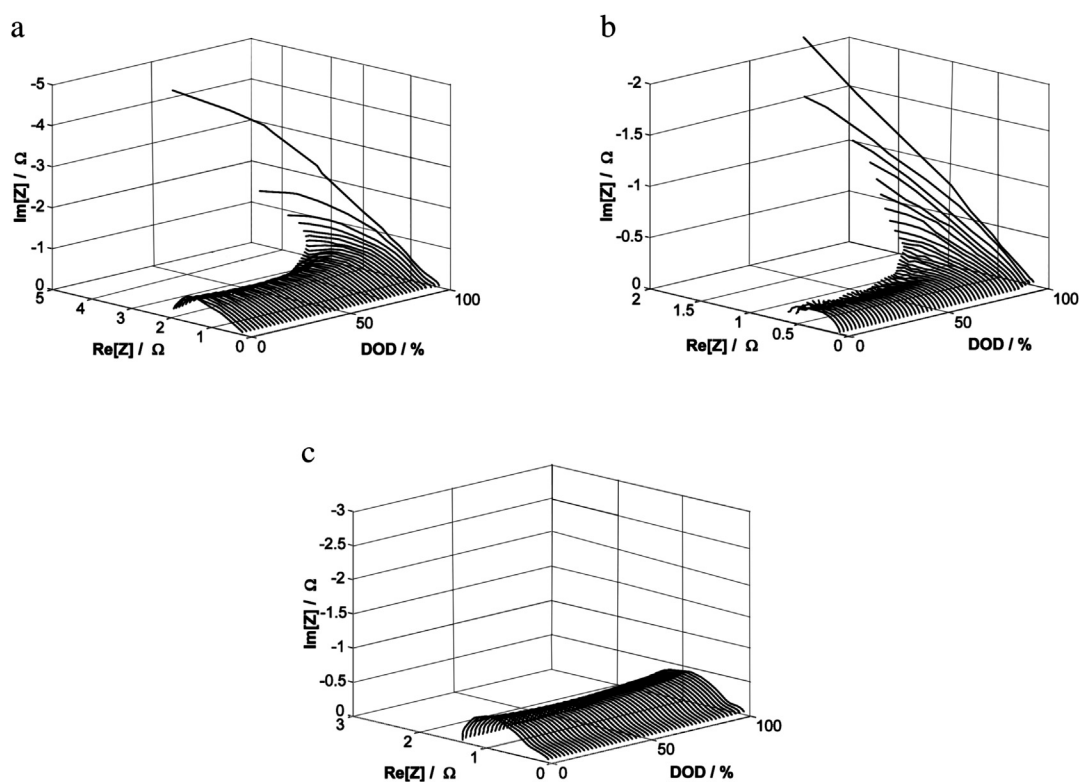


Fig. 3. a. An impedance characteristic curve of the entire cell whose capacity depends on the state of the positive electrode (in the function of DOD). b. An impedance characteristic curve of the positive electrode of the cell whose capacity depends on the state of the electrode (in the function of DOD). c. An impedance characteristic curve of the negative electrode cell whose capacity depends on the state of the electrode (in the function of DOD).

As for the positive electrode, it is visible that there is a characteristic increase in impedance towards the end of charging process which is associated with complete reduction of NiOOH to Ni(OH)_2 [8], while impedance values in the impedance graph representing the behaviour of the negative electrode are maintained at the same level during the entire cell discharge cycle. Such behaviour clearly proves that only the positive electrode is responsible for discharging the entire cell. Such a conclusion, however, cannot be drawn from the impedance characteristic curve obtained for the entire cell (see Fig. 3a).

In order to confirm that the collected conclusions were right, the third experiment was carried out on the basis of the second experiment. The negative electrode was charged partially prior to discharging the cell. However, spectra illustrating changes in impedance of the entire cell (Fig. 4a) do not support that fact. Nothing but an analysis of impedance characteristic curves of individual electrolyte materials offers such a possibility.

The value of impedance of the positive electrode during discharging does not change significantly (Fig. 4b), and as such it proves the partial discharge of the electrode, whereas the value of impedance of the negative electrode increases rapidly at the highest DOD values (Fig. 4c), which means that only the condition of the negative electrode is responsible for discharging the entire cell.

4. Discussion

By analysing the spectra of positive electrode impedance characteristic curves (Figs. 2b, 3b and 4b) it can be observed that they take the form of single flattened semicircles. Therefore, the spectra were analysed in accordance with the equivalent circuit presented in Fig. 5a.

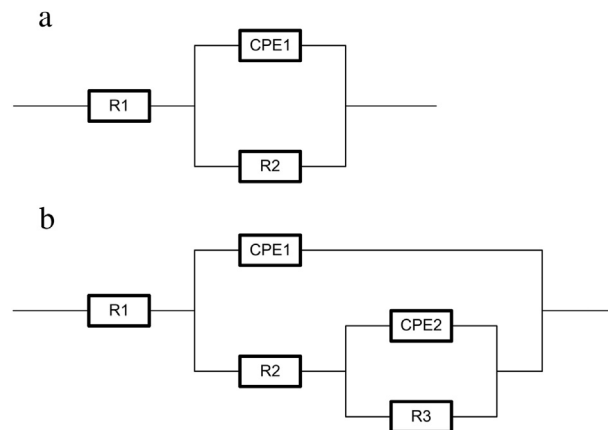


Fig. 5. a. Equivalent circuit model for the positive electrode. b. Equivalent circuit model for the negative electrode and the entire cell.

The spectra which represent the negative electrode (Figs. 2c, 3c and 4c) consist not one but two time constants. The first time constant occurs within the range of the highest frequencies and does not change during cell discharging. Most often it is associated with aspects such as resistance–capacitance characteristics between the reference electrode and the tested one, the contact between particles of the active material and the current collector, and properties of a hydride surface layer, etc. [20,21]. The second time constant, which occurs within low frequencies, increases the value as the electrically active material becomes discharged. The authors associate the fact with electrochemical processes which take place in the electrode [22]. Therefore, the spectra were analysed in accordance with the equivalent circuit presented in Fig. 5b.

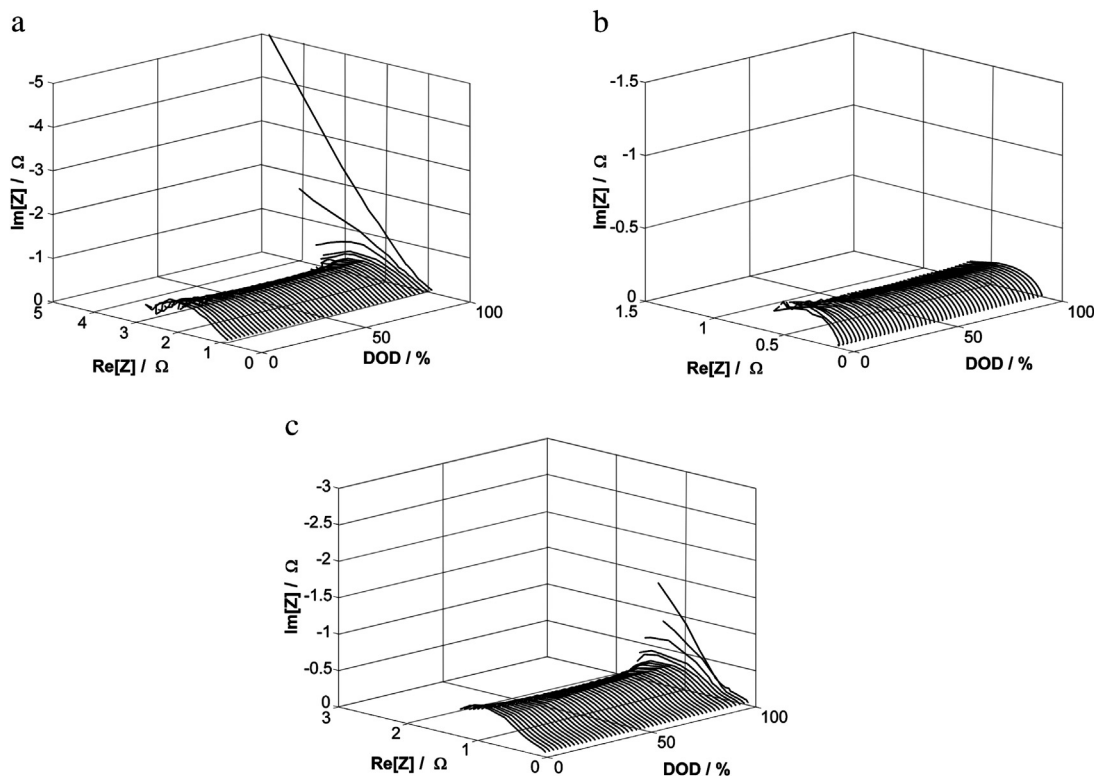


Fig. 4. a. An impedance characteristic curve of the entire cell whose capacity depends on the state of the negative electrode (in the function of DOD). b. An impedance characteristic curve of the positive electrode of the cell whose capacity depends on the state of the negative electrode (in the function of DOD). c. An impedance characteristic curve of the negative electrode of the cell whose capacity depends on the state of the electrode (in the function of DOD).

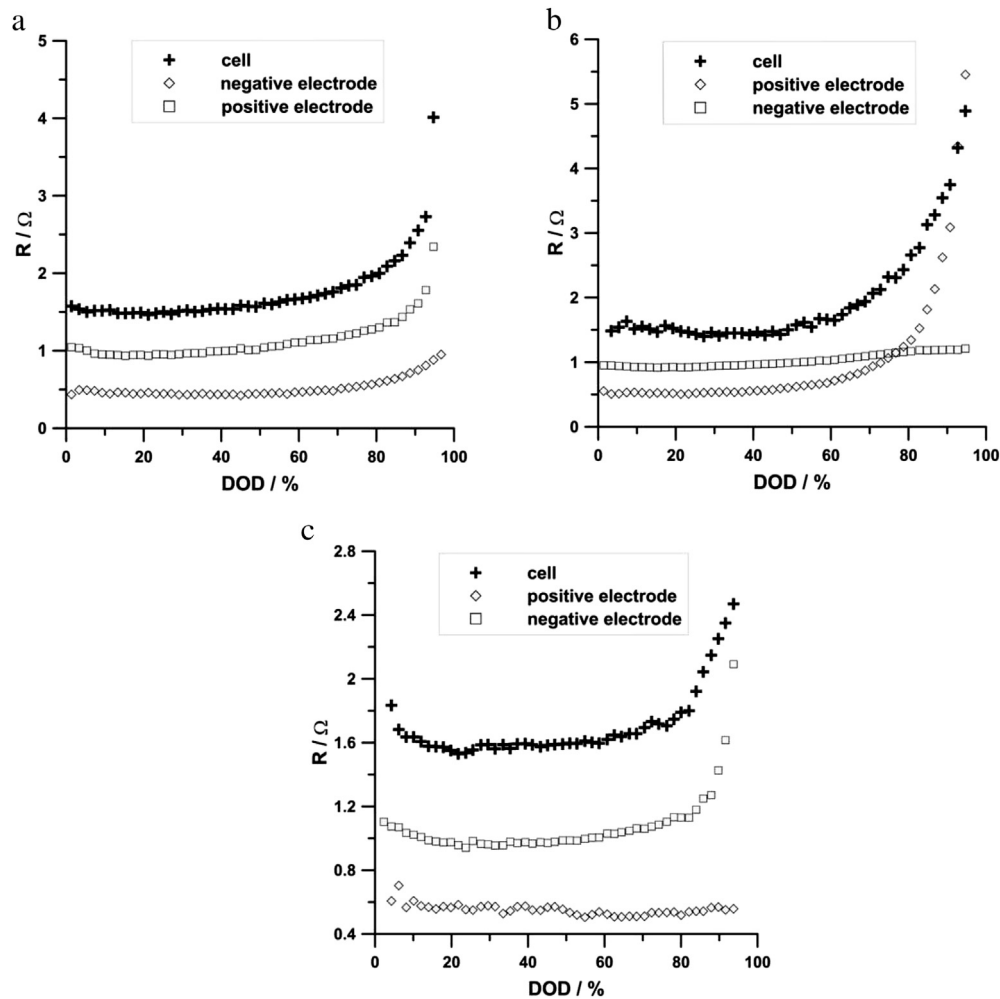


Fig. 6. a. Dependence of the resistance of individual components in the cell from experiment #1 in terms of cell discharge. b. Dependence of the resistance of individual components in the cell from experiment #2 in terms of cell discharge. c. Dependence of the resistance of individual components in the cell from experiment #3 in terms of cell discharge.

In view of the fact that one time constant can be distinguished within the equivalent circuit which represents the positive electrode, whereas there are two time constants for the negative electrode, it can be expected that the equivalent circuit describing the entire cell would have as many as three time constants. An analysis with three time constants did not lead to satisfying results. For this reason, a simplified circuit was applied, the same as for the negative electrode (see Fig. 5b).

By analysing the shape of the impedance spectra (Figs. 2a, 3a and 4a), there are two semicircles where the first occurs at high frequencies, whereas the second one at low frequencies. A further analysis was devoted to resistance within the range of low frequencies, which is associated by the authors with charge transfer resistance. Changes in the resistance for every electrically active element of the cell, as well as the entire cell during discharging are presented in Fig. 6a–c for the aforementioned elements from experiments nos. 1, 2, and 3 respectively.

Fig. 6a shows a correlation between the change in resistance of the entire cell during discharging and changes in charge of transfer resistance for the positive and the negative electrodes during the same process. It can be observed that the resistance of the entire cell is a sum of positive and negative electrode resistance values.

By taking a closer look at Fig. 6 it is possible to notice that an increase in charge transfer resistance, as determined for the entire cell, practically corresponds with the resistance obtained for the

positive electrode which was charged partially with reference to the negative electrode whose resistance is constant during complete discharging of the cell.

A summary of resistance changes during discharging as in the last experiment reveals an increase in resistance of the negative electrode (it was charged partially prior to discharging), to the same extent as an increase in resistance of the entire cell, along with a progressing discharge (Fig. 6c). Resistance of the positive electrode remains at the same level during the entire discharge cycle, and as such it means that it has been discharged partially and does not condition operation of the entire cell.

5. Conclusions

The presented results obtained during cell discharging under various conditions of the electrodes unambiguously indicate that both the impedance of the positive, as well as negative electrodes, cannot be passed over. A simple spectrum form obtained within the dual-electrode measurement can be in fact a complicated waveform containing several time constants. A proper impedance-oriented analysis of the battery should be based on spectra of the positive and negative electrode.

Impedance monitoring of the cell on the basis of dual-electrode measurement can be employed in assessing its state of discharge. In order to obtain detailed information on which electrode is

responsible for the condition of the entire cell at a given moment, or what kind of processes are taking place, a simultaneous and continuous measurement of impedance values of all secondary cell electrodes is necessary.

Acknowledgements

The authors acknowledge the financial support from the Ministry of Science and Higher Education (Poland) under Grant 2012/05/N/ST8/02918.

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