Int. J. Electrochem. Sci., 11 **(2016)** 8927 – 8937, doi: 10.20964/2016.11.67

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Application of Modified with Copper Porous Carbon Matrix on Lead-Acid Battery

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Received: 9 August 2016 / *Accepted:* 22 September 2016 / *Published:* 10 October 2016

Negative plates for the lead-acid battery with porous carbon grids coated with cooper or copper and lead have been prepared and tested. In the first stage of the study a method of galvanic coating of the porous carbon matrix was developed. Analysis of the quality of the metal coatings was based on the results obtained with a scanning electron microscope. Measurement of the electrical conductivity for a series of collectors modified with various metal layers was also performed. Additionally, for the carbon matrix modified with a double metal layer of 20 μm Cu and 20 μm Pb a series of electrochemical measurements using cyclic voltammetry was performed to investigate its electrochemical properties and compared with a solid lead electrode. In the study a series of experimental cells was prepared in which the negative plate collector used: an unmodified carbon matrix, a carbon matrix modified with lead or copper and a carbon matrix modified with double metal, copper-lead layer.

Keywords: lead-acid battery, negative plate, carbon matrix, copper-lead

1. INTRODUCTION

The lead-acid battery still remains one of the most widely used electrochemical power sources. They range from the extremely large battery systems used in load leveling by electrical utility companies to the relatively small batteries used in hand tools. A promising approach to increase the relatively low specific energy and capacity of lead-acid batteries is the use of lightweight porous carbon materials, coated with metals, as current collectors.

As an alternative for lead alloys, reticulated vitreous carbon (RVC) has been proposed and examined by Czerwiński as a grid material [1-3]. This lightweight, conductive, porous carbon material in a 3% apparent density of it is parent material carbon, so it is ca. few times lower in comparison to lead alloys [4-5]. Czerwiński and co-workers constructed lead-acid batteries using RVC as a current collector and carrier for active mass for both negative and positive plates. In other studies [6-8] it has been demonstrated that RVC covered and non-covered with thin Pb layer (20 μm) has excellent behavior as a carrier and current collector in the negative plate of the lead-acid battery. The charging-discharging behavior and Peukert's plots of both collectors were very similar. However, the collector covered with lead has better mechanical characteristics. Gyenge et al. used RVC plated with a thick Pb-Sn layer (80-100 μm) as the negative plate grid [9-10]. Their cell completed over 300 cycles at 25% depth of discharging. Dai and co-workers proposed copper foam modified with lead as a negative plate current collector [11-12]. Examined electrode material indicated good stability in the negative plate potential range after 100 cycles polarization.

In conventional lead-acid batteries the copper components are applied in the composite grids [13-14]. A typical composite grid contains a copper layer or core. Copper components are always located deep enough below the free surface such that they are not exposed to the electrolyte during the life time of the battery. The use of copper components decreases the resistivity and, improves the electrical properties and the performance parameters significantly.

There are some studies on carbon based current collectors modified with copper, but they mainly concern the positive plate grid. Ji and co-workers used copper foam modified with lead as the carrier and current collector in the positive plate [15]. Copper foams were prepared by subjecting polyurethane foams to pre-treatment followed by electro-less copper plating and heat treatment. The copper foams were then used as substrates to prepare lead foams by the electroplating process. The charging voltages of the lead-foam batteries were lower, while discharging voltages were higher than that of the cast-grid batteries. Kirchev published a lead-acid battery design employing a glassy carbon slab covered with cooper and lead-tin alloy as the plate grid [16]. In his presented current collector only the electrical contact was covered with copper to increase the electrical conductivity.

In this paper, carbon foam grids were successfully modified by electrodeposition of copper, lead, or double-metal layer: copper-lead. It was developed a negative plate current collector based on carbon matrix modified with copper with improved electrical and mechanical properties. Copper in comparison to the lead have a considerably higher electrical conductivity and hardness, so it follows that with constant cross section the electrical conductivity and the mechanical strength of current collector can be increased. These grids performance in an experimental battery was investigated by means of scanning electron microscope (SEM), cyclic voltammetry and galvanostatic charging/discharging tests.

2. EXPERIMENTAL

RVC® with 20 ppi (pores per inch) porosity grade, purchased from ERG Material and Aerospace Corporation was chosen as the most suitable for this research. The plates were prepared from an RVC block which was cut into small pieces with average dimensions 40 mm x 20 mm x 5 mm. The electrical contact between Pb and RVC was casted using melted lead. Series of experimental negative plate collectors were prepared: unmodified carbon matrix (RVC), carbon matrix modified with lead (20 µm) (Pb/RVC) or copper (20 µm) (Cu/RVC) and carbon matrix modified with double-metal, copper-lead layer (20 µm / 20 µm) (Pb/Cu/RVC). RVC plated with a Pb layer (100 µm) was used as the positive plate grid. Carbon substrates were modified by electroplating. The electroplating of copper was conducted in the sulphate bath [17] and the lead in the methane sulfonate bath. The thicknesses of the Cu and Pb layers were calculated from deposit weights and the real surface area of the RVC [5]. The calculation was in agreement with obtained SEM pictures.

Table 1. Thickness of Cu and Pb layers.

Current collectors		Thickness of metal layer [μm]	
		Cu	Pb
Negative plate grid	RVC	-	-
	Pb/RVC	-	18
	Cu/RVC	19	-
	Pb/Cu/RVC	19	19
Positive plate grid	Pb/RVC	-	97

Morphologies of the copper and lead layers surfaces were examined with a JEOL JSM-6490LV scanning electron microscope (SEM).

Tightness and stability of the lead layer in the carbon matrix modified with double-metal, copper-lead layer was tested by cyclic voltammetry after they were degreased and cleaned. The cyclic voltammetry tests were carried out using a CHI604C electrochemical workstation, which was connected to the examined collector set as the working electrode, a lead plate set as the counter electrode and a Hg/Hg_2SO_4 electrode set as the reference electrode. The electrolyte was a 4,9 M (37,5 wt %) Hg_2SO_4 solution.

The electrical conductivity of all studied negative current collectors was compared. Electrical conductivity was calculated from the difference of potential between two points (distance is 20 mm) on the collector under passage of a constant current of 1 A. Measurements were carried out using an AMREL LPS 303 laboratory power supply and SANWA PC510a multimeter. Figure 1 presents a scheme of the measuring system.

Examined grids were pasted with a standard SLI-type paste used in lead-acid battery. The nominal capacities of the negative and positive active masses were 145 Ah kg^{-1} and 120 Ah kg^{-1}, respectively. The average amount of the paste pressed into each collector was between 13 and 16 g (1.89 – 2.32 Ah) for the negative plates and between 12 and 14 g (1.44 – 1.68 Ah) for the positive plates. Plates were then subjected to a two-step curing process lasting 12 h at 50 ºC and at 90% relative humidity and drying at 60 ºC for the next 24 h. To form the battery, the positive-negative-positive configuration was used, wherein the examined negative plate was sandwiched by two positive plates (Fig. 2). In this configuration, the battery capacity was limited by the negative plate capacity. Both positive plates were separated from the negative one with a PP envelope-type separator. After soaking for 1 h in 2.3 M (20 wt %) H_2SO_4 electrolyte forming was conducted at a constant current of 0.067C for 60 h. After formation, acid concentration was adjusted to 4.9 M (37.5 wt %) H_2SO_4. Discharging tests at different current rates in the range 0.05-3 C were performed using an ATLAS 1361 battery tester. The cutoff voltage during the discharging was 1.75 V for currents below 0.5 C and 1.6 V for currents over 0.5 C. Constant-current charging was performed with a 0.05 C current hold for 24 h.

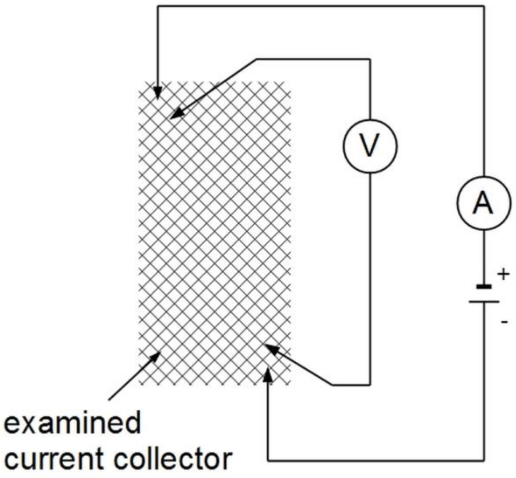

Figure 1. Scheme of the system for measuring the electrical conductivity.

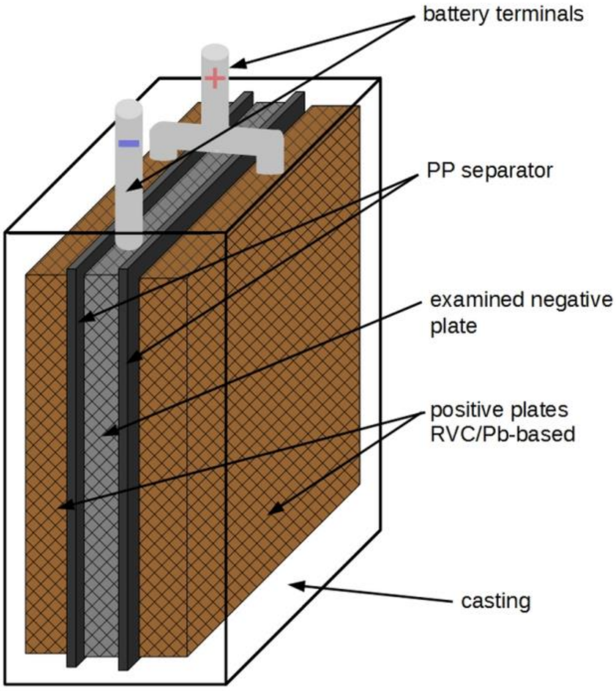

Figure 2. Scheme of three-plate lead-acid cell for negative plate testing.

3. RESULTS AND DISCUSSION

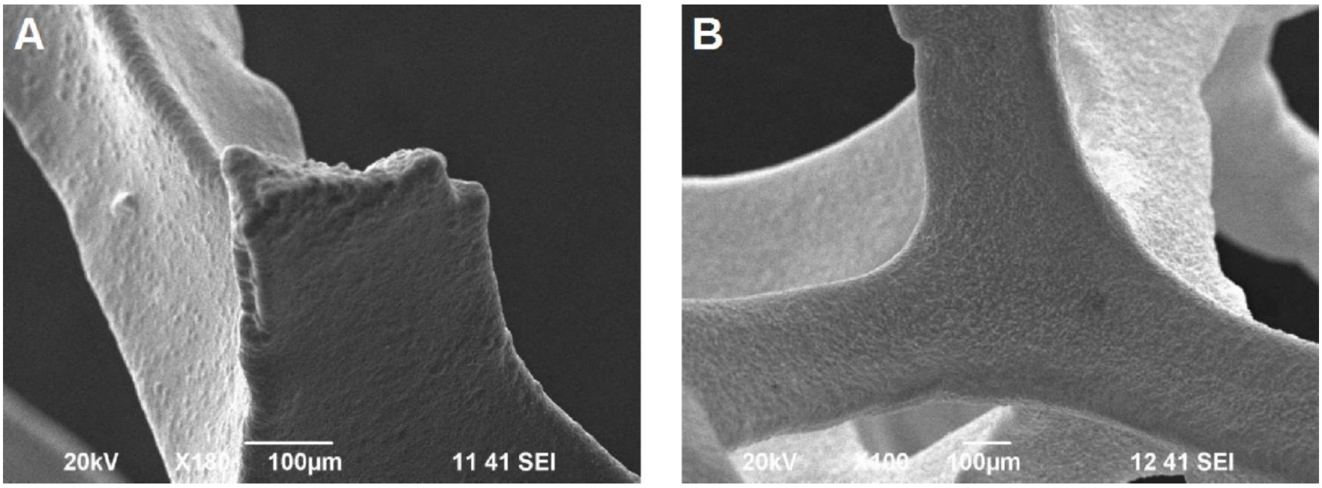

Figure 3. SEM images of RVC matrix modified with copper (A) and double-metal, copper-lead layer(B).

Fig. 3 shows SEM images of the RVC matrix electroplated with copper and double-metal copper-lead layer. It is visible that tight deposits fully covering the substrate were obtained. The smooth surface of the copper layer facilitates obtaining an optimum coverage of lead during the lead electroplating process. Fig. 4 presents an SEM image of a cross-section of the electroplated RVC matrix. The image shows that the electrodeposited lead has good contact with the copper layer. The lead coating will supposedly protect the copper substrate against damage by electrolyte penetration and leaching of copper.

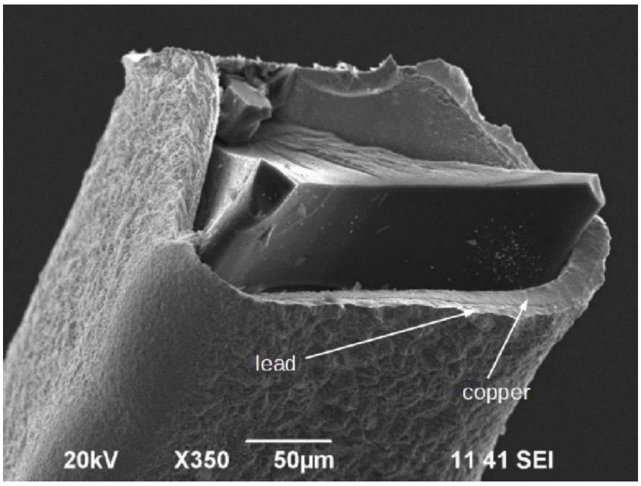

Figure 4. SEM image of a cross-section of the RVC matrix modified with double-metal copper-lead layer.

The tightness of the Pb layer and the general electrochemical behavior of the Pb/Cu/RVC electrode was examined by cyclic voltammetry. Fig. 5 presents a cyclic voltammogram recorded for the Pb/Cu/RVC electrode in the full potential range. The well-known features are visible: oxidation of Pb to $PbSO_4$ (anodic currents at ca. -0.9 V), oxidation of $PbSO_4$ to PbO_2 and the evolution of O_2 (anodic currents above at ca. 1.6V), reduction of PbO to $PbSO_4$ (cathodic currents at ca. -1.0 V) and reduction of $PbSO_4$ to Pb (cathodic currents below ca. -1.1 V) [18]. There were no current signals belonging to the Cu/Cu^{2+}. The CV curve is very similar to that for the solid Pb electrode. For comparison, a CV curve for the solid Pb electrode is show in Fig. 5. Conclusion can be drawn that there was no copper dissolving and the degree of hydrogen evolution did not increase.

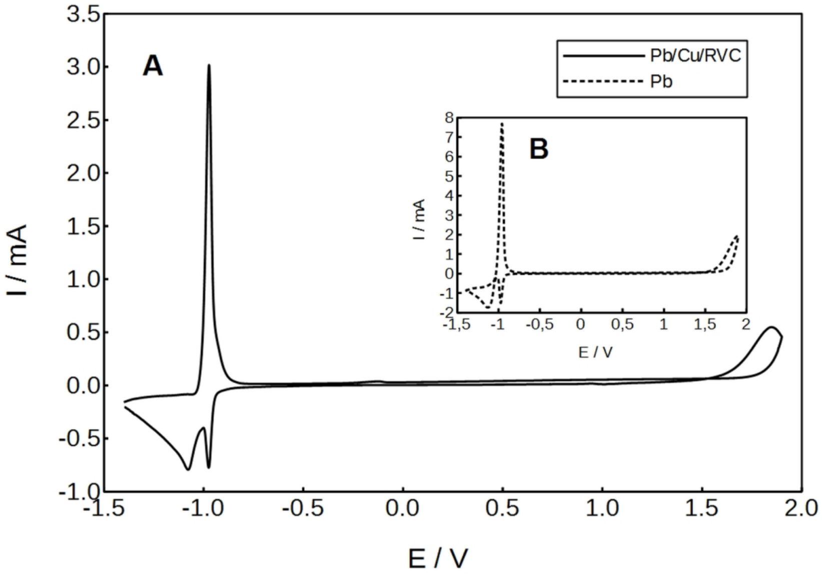

Figure 5. Cyclic voltammogram in 4.9 M (37.5 wt %) H_2SO_4 in the full potential range (-1.4 to 1.9 V), scan rate 0.05 V s^{-1} for Pb/Cu/RVC electrode (A) for solid Pb electrode (B).

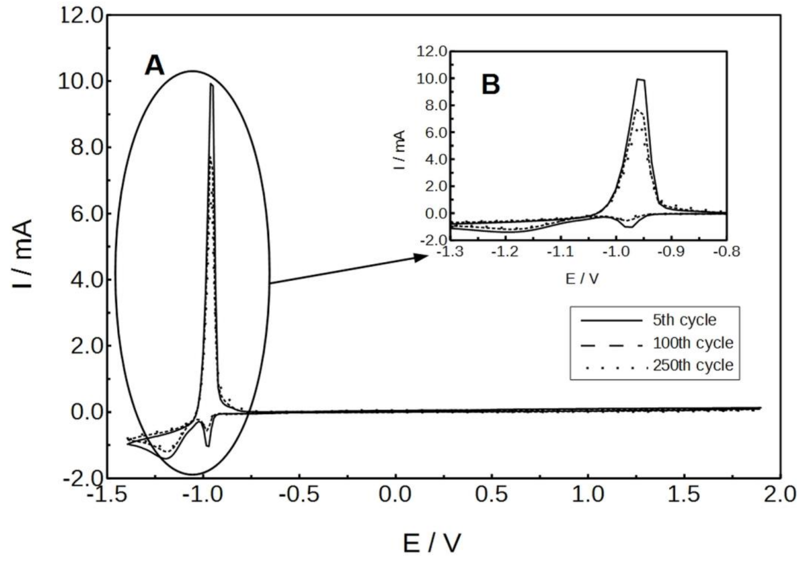

Figure 6. Cyclic voltammograms (0.5 V/s) for Pb/Cu/RVC electrode subjected to continuous potential cycling in 4.9 M (37.5 wt %) H_2SO_4 (A). Sulfate region in greater detail (B).

Fig. 6 shows CV curves recorded for the Pb/Cu/RVC electrode during continuous potential cycling. This procedure was applied to check the stability of the double-metal layer covering the RVC matrix. No significant deterioration of the tightness of the Pb layer was observed even after 250 cycles, i.e., there were no current signals detected connected with the oxidation/reduction of copper. Comparing Fig. 5 with Fig. 6 one should note some differences in the oxidation of $PbSO_4$ and the O_2 evolution currents. In Fig. 5 anodic current was observed above ca. 1.6V while in Fig. 6 the anodic peak was not present. The differences between both CV curves originate from different scan rates applied. Fig. 5 shows a lower scan rate (0.05 V/s) than Fig. 6 (0.5 V/s).

A comparison of the electrical conductivity of the examined current collectors is shown in Table 2.

Table 2. Electrical conductivity of examined current collectors.

Current collectors	Thickness of metal layer [μm]		Electrical conductivity of similar samples [kS]
	Cu	Pb	
RVC	-	-	0.4
Pb/RVC	-	18	115
Cu/RVC	19	-	1429
Pb/Cu/RVC	19	19	1563

Data presented in Table 2 shows that the electrical conductivities of the RVC matrix modified with copper and double-metal, copper-lead layer were very similar. The electrical conductivity of the RVC matrix modified with copper was more than ten times higher than for the RVC matrix modified with lead and more than three thousand times higher than unmodified RVC matrix. Applied copper layer significantly increased the electrical conductivity. Moreover obtained results indicate that the conductivity of the Pb/Cu/RVC sample was determined by the conductivity of copper layer.

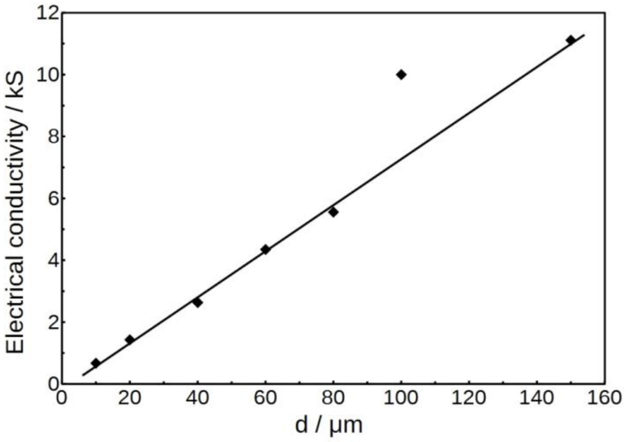

Figure 7. Dependence of electrical conductivity on thickness of the copper layer (d) for Cu/RVC.

Fig. 7 shows the dependence of the electrical conductivity on the thickness of the copper layer for the RVC matrix modified with copper in the thickness range of the copper layer from 10 to 150 µm. It can be noted that the dependence of electrical conductivity on the thickness of the copper layer is linear all over the investigated range.

To compare the performance of the RVC matrix modified with copper and double-metal, copper-lead layer with the RVC matrix modified with lead and the unmodified RVC matrix, the charging/discharging properties of the batteries employing these collectors as in the negative plate were investigated. In order to determine the specific capacity of the negative active mass the cell was subjected to discharging/charging cycle at a discharging current of 0.05 C (20 h of discharging mode) while charging was performed for 24 h with 0.05 C current. The specific capacity of all prototype cells (calculated only from active mass) prepared varied between 158 and 162 Ah kg^{-1} (Table 3). The obtained values were very similar and about 10% higher than the nominal capacity of the negative active mass used. Moreover, they were in agreement with other research focusing on reticulated collectors [6-8, 19-20].

Table 3. Physical characteristics of examined negative plates.

Cell	Current collector	NAM mass [g]	γ [g cm^{-2}]	Capacity to NAM [Ah kg^{-1}]
A	RVC	15.4	0.26	159
B	Pb/RVC	14.2	0.26	158
C	Cu/RVC	13.1	0.26	162
D	Pb/Cu/RVC	15.7	0.27	159

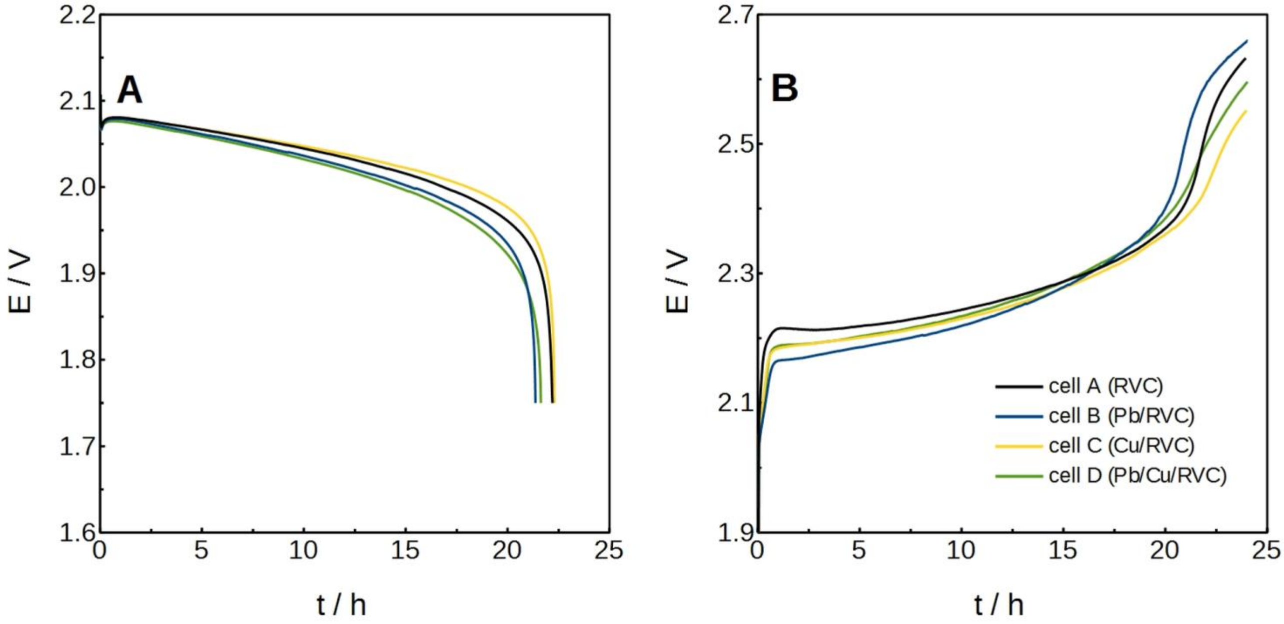

Figure 8. Discharging (A) / charging (B) characteristic of different batteries at constant discharging/charging current 0.05 C.

Table 3 shows masses and capacities of NAM and the electrode design factor γ of the examined negative plates. γ is the ratio of the active mass to the collector surface area (g cm^{-2}). Value of the factor γ was very similar for all examined current collectors. Moreover, obtained values were comparable with other research focusing on reticulated collectors [9, 11, 15, 19] and significantly lower than γ factor of typical lead-acid batteries (2.0 – 2.5 g cm^{-2}) [21].

Fig. 8 presents the discharging/charging profiles of prototype batteries. The voltage level during discharging at 0.05 C was stable and similar for all cells. The initial charging voltages of the different batteries were close to each other. However, during charging with the constant current of 0.05 C over for 20 h, the batteries employing RVC modified with copper showed a lower charging voltage than the other ones, and this gap remained until the end of charging time (Fig. 8B). Since the hydrogen evolution reaction in the batteries with the Cu/RVC and the Pb/Cu/RVC collectors occurred at a later time than in the battery with the RVC and the Pb/RVC collectors. The lower polarization during charging in batteries with RVC modified with copper indicated that they could be charged with higher current rate at the same voltage. On the other hand the applied modification allows to reduce the problem of low loading efficiency, water loss and heat. A similar effect was observed for cast grid modified with copper [22].

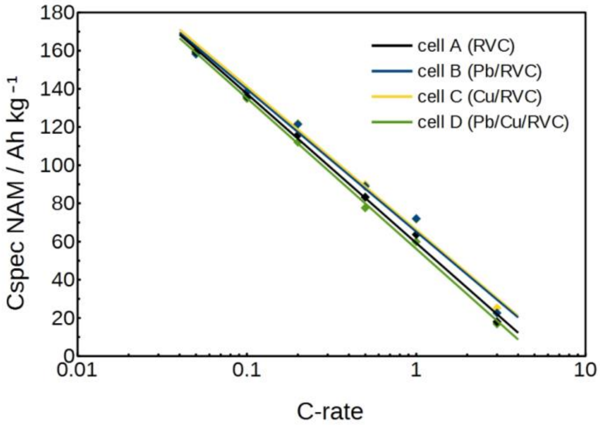

Figure 9. Dependence of apparent specific capacity on discharging current for different batteries.

In Fig. 9 the Peukert dependencies for lead-acid batteries with RVC (cell A), Pb/RVC (cell B), Cu/RVC (cell C) and Pb/Cu/RVC (cell D) based negative plates are demonstrated. The plots for all types of electrodes exhibit very similar behavior. In the considered range of discharging currents (0.05 C – 3 C) apparent capacities related to the negative active mass in the negative plates based on RVC, Pb/RVC, Cu/RVC and Pb/Cu/RVC carrier-collectors were comparable.

4. CONCLUSIONS

The RVC matrix could be modified by electroplating with copper and twin layer of metals (Cu-Pb). The obtained deposit is tight and fully covered the substrate. The Pb/Cu/RVC electrode exhibited electrochemical properties typical of the solid lead and no significant deterioration of tightness of the Pb layer was observed even after 250 polarization cycles in the full potential window (-1.4 to 1.9 V).

The electrical conductivity of the RVC matrix modified with copper was more than ten times higher on comparison to RVC matrix modified with lead and more than three thousand times higher than for the unmodified RVC matrix.

It was developed a negative plate current collector based on carbon matrix modified with copper with improved electrical and mechanical properties. Examined collectors showed properties typical for three-dimensional current collectors (increased specific capacity, low factor γ).

Discharging/charging measurements of battery palates based on RVC matrix modified with Cu and Pb indicated that the specific capacity of all prototype cells varied between 158 and 162 Ah kg^{-1} (Table 3) and was simultaneously about 10% higher than the nominal capacity of the negative active mass used. Also Peukert dependencies showed that negative plates constructed with Cu/RVC and Pb/Cu/RVC as the carrier and the current collector had good electrochemical behavior in a wide range of discharging current (from 0.05 to 3 C). The results prove that both examined collectors (Cu/RVC and Pb/Cu/RVC) can be used as a current collector in negative plates of lead-acid batteries.

The lower polarization during charging in batteries with RVC modified with copper indicated that these batteries could be charged with higher current rate. The applied modification allows to reduce the problem of low loading efficiency, water loss and heat.

ACKNOWLEDGEMENTS
This work was financially supported by the Industrial Chemistry Research Institute through project 841333.

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