Short communication

Hybrid lead-acid battery with reticulated vitreous carbon as a carrier- and current-collector of negative plate

A. Czerwiński [a,b], S. Obrębowski [a,b], J. Kotowski [b], Z. Rogulski [a,b,*], J. Skowroński [c], M. Bajsert [d], M. Przystałowski [d], M. Buczkowska-Biniecka [d], E. Jankowska [e], M. Baraniak [e], J. Rotnicki [e], M. Kopczyk [e]

[a] Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland
[b] Warsaw University, Department of Chemistry, Pasteura 1, 02-093 Warsaw, Poland
[c] Poznań University of Technology, Piotrowo 3, 60-965 Poznań, Poland
[d] JENOX Ltd., Notecka 33, 64-800 Chodzież, Poland
[e] IMN Central Laboratory of Cells and Batteries, Forteczna 14, 61-362 Poznań, Poland

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ABSTRACT

Bare reticulated vitreous carbon (RVC) plated electrochemically with thin layer of lead was investigated as a negative plate carrier- and current-collector material for lead-acid batteries. Hybrid flooded single cell lead-acid batteries containing one negative plate based on a new type (RVC or Pb/RVC) of carrier/current-collector and two positive plates based on Pb–Ca grid collectors were assembled and subjected to charge/discharge tests (at 20-h and 1-h discharge rates) and Peukert's dependences determination. The promising results show that application of RVC as carrier- and current-collector in negative plate will significantly increase the specific capacity of lead-acid battery.

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1. Introduction

Lead-acid batteries production needs relatively simple and cheap technology, therefore, LABs are still the best choice for many medium and large-scale energy-storage applications. The main disadvantage of lead-acid battery system is low specific capacity compared to other battery systems. For all existing and prospective applications of lead-acid batteries a significant gain to specific capacity is highly desirable. The main reason of this property is the high contribution of lead alloys carrier (plate grid) in the total mass of negative and positive plates. The solution proposed by Czerwiński [1–4] was to use reticulated vitreous carbon (RVC) as based current- and carrier-collector for active mass as an alternative to lead based alloy grids. Czerwiński's idea to use RVC as a carrier- and current-collector for lead-acid batteries was adapted further by Gyenge et al. [8,9] who constructed lead-acid battery using RVC covered with lead alloys as a current-collector for both negative and positive plates. Other than RVC types of reticulated carbon materials can also be used as a current-collector in lead-acid batteries. Carbon foam prepared by carbonization of petroleum-derived pitch was evaluated by Chen and co-workers. Extensive examinations proved, that this type of carbon foam can be successfully prepared, plated with lead, pasted and worked under cyclic conditions in lead-acid battery system [10–13].

RVC is lightweight foam-like, conductive glassy carbon material [15–17]. It has continuous structure and density as low as $1.5\,\mathrm{g\,cm^{-1}}$ ($0.05\,\mathrm{g\,cm^{-1}}$ including void volume) which is ca. few times lower in comparison to lead alloys. It has been found also that electrochemical properties of RVC covered with thin layer of lead do not differ from those of pure bulk lead [2–7,16]. Using RVC-based carrier and collector leads to significant drop of electrode mass. Typical lead carrier and collector makes up ca. 40% of the mass of dry plate [14].

In this paper a new construction of lead-acid battery and its performance is demonstrated. Complete lead-acid battery containing one negative, RVC-based plate and two positive plates have been assembled. One can see significant weight decrease of plates with RVC-based carrier and current collectors without changes of stored energy.

* Corresponding author at: Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland. Tel.: +48 22 5682447.
E-mail address: zbigniew.rogulski@ichp.pl (Z. Rogulski).

Fig. 1. Negative RVC-based lead-acid plate.

2. Experimental

The negative plate was prepared from 20 ppi (pores per inch) RVC block which was cut into small substrates with average dimensions 40 mm × 25 mm × 3 mm. Electrical contact was made from bunch of thin Pb wires ($d = 0.5$ mm). Average weight of the RVC substrate with electrical contact was varied between 1.4 and 1.6 g. The substrates were divided into two batches. One batch of substrates was plated electrochemically with lead from alkaline acetate bath. The other was left to further examination without lead plating. In the next step substrates were pasted manually with fresh negative paste obtained from JENOX Ltd. lead-acid battery manufacturer. Plates were then subjected to two-step curing process lasting 24 h in 45 °C at 90% relative humidity and drying in 45 °C for the next 24 h. The amount of active mass in negative plates after process of curing was between 11 and 15 g (±0.5) g. For better performance and maximum charging–discharging efficiency of negative plate we have designed an experimental cell with two positive plates. Complementary positive plates were cut out from traction 60 Ah 12 V JENOX battery plates to meet the dimensions of RVC-based negatives. 2 V plate stacks were assembled with one negative RVC-based plate put between two positive plates to ensure that battery capacity is limited with negative plate capacity. Fig. 1 shows one negative plate. For better performance and maximum charging–discharging efficiency of negative plate the amount of positive active mass in positive plates was doubled in comparison to negative active mass.

Both positive plates were separated from the negative one with PP envelope type separator (Fig. 2). A single plate stack was supported with PVC spacers on the sides, placed in plastic casing. Such prepared cells were flooded with exceed of 1.15 g cm^{-3} sulphuric acid.

After soaking for 4 h in H$_2$SO$_4$ electrolyte with $d = 1.15$ g cm^{-3} at the temperature of 40 °C formation process was conducted with 100 mA formation current. For estimation of formation and initial charging–discharging current nominal capacity of all experimental cells was estimated at the level of 1.3 Ah per cell (118 mAh g^{-1} NAM). Discharge tests at different current rates and cyclic charge/discharge tests at 1.00 A current rate were performed in H$_2$SO$_4$ electrolyte with $d = 1.26$ g cm^{-3} using Bitrode SCN battery tester. The cyclic procedure of 1 h discharge mode was as follows:

cell discharging at 1.00 A to voltage cut equal to 1.6 V
cell left at open circuit for 30 min
cell charging at 0.16 A for 12 h
1 min at open circuit before the next discharging step.

3. Results

In order to determine nominal capacity of the cell after its formation the cell was subjected to three charge/discharge cycles at discharge current 80 mA (20 h of discharging mode, 0.05 C) while charging was performed for 12 h with 160 mA current. Table 1 shows selected 0.05 C capacities for experimental cells obtained in the 3rd cycle after formation process. Values are related to negative active mass and complete plate mass together with carrier and Pb wire collector. 20-h capacities of cells based on Pb/RVC and bare RVC collectors are comparable and vary between 135 and 155 mAh g^{-1} NAM. Average value of capacity for batch containing 14 electrodes is 146 mAh g^{-1} NAM which is in agreement with the data of the producer (JENOX Ltd.). This value is taken as nominal.

Figs. 3 and 4 demonstrate discharge characteristics in semi-logarithmic scale for different current rates for lead-acid cell with negative plate based on Pb covered RVC carrier-collector (Pb/RVC) (Fig. 3) and for negative plate of lead-acid cell with bare RVC carrier-collector (Fig. 4).

Figs. 3 and 4 show clearly that the discharge parameters for lead-acid battery with RVC and Pb/RVC carriers are virtually the same as for flooded batteries with regular cast grids. When comparing potential-time discharge characteristic it can be assumed that there are no significant differences between discharge performances of the cell with Pb covered with RVC carrier-collector and the cell with bare RVC carrier-collector for currents between 0.05 and 1 C.

To show the usefulness and performance of lead-acid battery as power source the Peukert's equation is used:

$$I^n t = C \tag{1}$$

where I stand for discharge current, t for discharge time and C for the capacity of the cell, Table 2 presents obtained Peukert's coefficients n for RVC and Pb/RVC supported negative plate samples
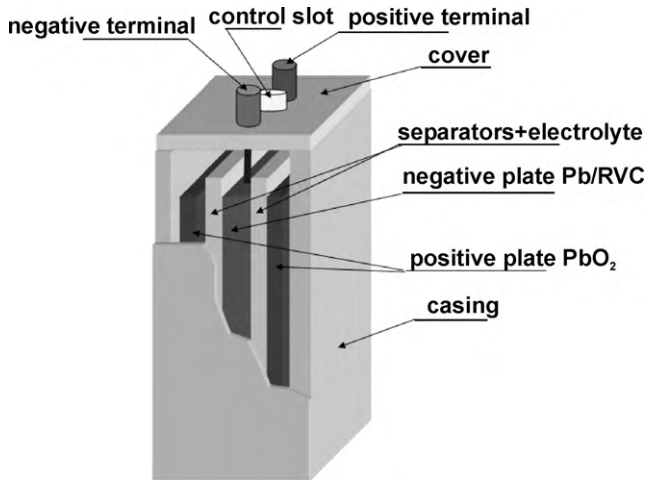
Table 1
Selected C20 capacities for experimental cells obtained in the 3rd cycle after formation process.

	Collector type	NAM mass	t_{20} (h)	Capacity to NAM (Ah kg^{-1})	Capacity to plate mass (Ah kg^{-1})	Average % of carrier and collector mass in plate	Average % of carrier and collector mass classic Pb alloy grid
1	Pb/RVC	10.82	20.4	149	131		
2	Pb/RVC	11.10	20.7	153	135		
3	Pb/RVC	10.52	20.7	146	128		
1A	RVC	13.47	22.6	144	129	12%	36–40%
2A	RVC	12.99	22.1	145	130		
3A	RVC	11.56	20.8	142	125		

Values are related to negative active mass and to plate mass. 20-h capacities of cells based on Pb/RVC and bare RVC carrier-collector are demonstrated.

Fig. 2. Scheme of lead-acid electrode cell with negative plate testing based on RVC carrier and current-collector.
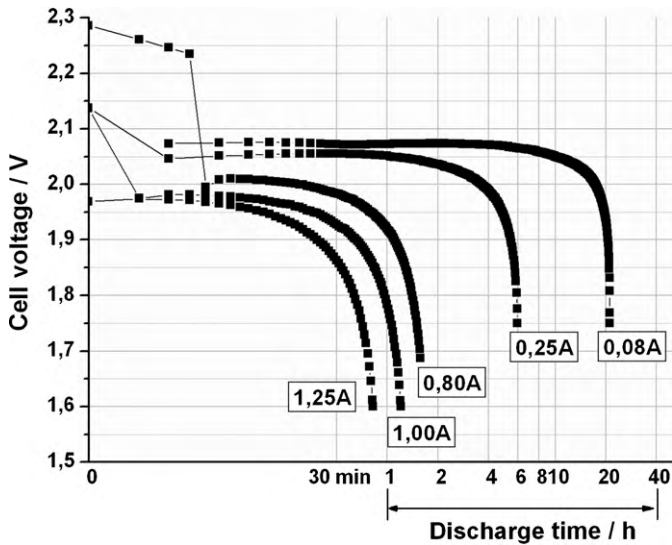

Fig. 3. Constant current discharge characteristics of lead-acid battery with Pb/RVC (sample 2) based negative plate.
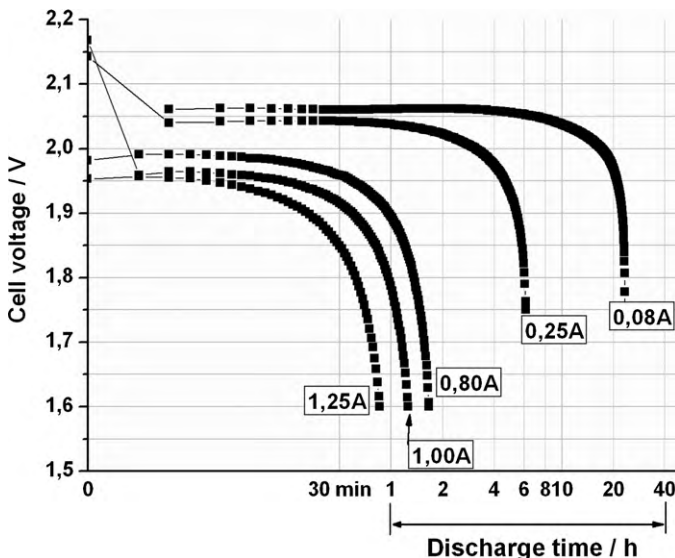

Fig. 4. Constant current discharge characteristics of lead-acid battery with RVC (sample 2A) based negative plate.

Table 2
Peukert's coefficients n for samples with RVC and Pb/RVC supported negative plates.

	Plate type	n-Peukert's coefficient	Average Peukert's coefficient for RVC and Pb/RVC-based plate (7 pcs batch)
1	Pb/RVC	1.285	1.309
2	Pb/RVC	1.217	
3	Pb/RVC	1.364	
1A	RVC	1.205	1.280
2A	RVC	1.244	
3A	RVC	1.489	

presented also in Table 1. For commercial lead-acid batteries typical parameters Peukert's coefficient is equal to 1.3. Average value of Peukert's coefficient found in all our experiments for negative plate with bare RVC equals to 1.280 and for plate with Pb/RVC carrier is equal to 1.309.

In Fig. 5 the plots $\log t$ vs. $\log I$ for electrodes with bare RVC (Fig. 5) and Pb/RVC with deposited Pb (Pb/RVC) are demonstrated. The plots of both kinds of electrodes show very similar behavior.

Figs. 6 and 7 show battery capacity change over deep charging–discharging cycles of selected cells with the discharge cut off voltage 1.6 V in 0.7 C (1.00 A) mode and with the discharge cut off voltage 1.75 V in 0.05 C mode. The carrier-collector of negative plates was Pb/RVC (Fig. 6) and RVC (Fig. 7). Both demonstrated electrodes has completed 47 cycles in different modes. For the first three cycles discharge current was 0.08 A (the third was taken for electrical capacity estimation of the particular cell), the next four discharge cycles were taken for Peukert coefficient calculation (0.25, 0.80, 1.00 and 1.25 A). Next 40 cycles were taken with 1.00 A (20 cycles) and with 0.08 A (20 cycles) discharge currents. The electrodes were permanently tested, i.e. without breaks per ca. 6 weeks.

The obtained results (see Figs. 6 and 7) showed that bare and covered with lead RVC are very well suitable for future studies as carrier- and current-collector in lead-acid batteries. Average values of specific 0.7 C (1 A) and 20 C (0.08 A) capacities related to negative active mass (NAM) of negative plates based on Pb/RVC and bare RVC carrier-collector are comparable. Average NAM capacities from 20 full charge–discharge cycles are 122 mAh g^{-1} (Pb/RVC-based plate) and 117 mAh g^{-1} (RVC-based plate) for 0.08A discharge rate. Relevant values for 0.7 C rate are 87 mAh g^{-1} NAM for Pb/RVC-based plate and 88 mAh g^{-1} for bare RVC.
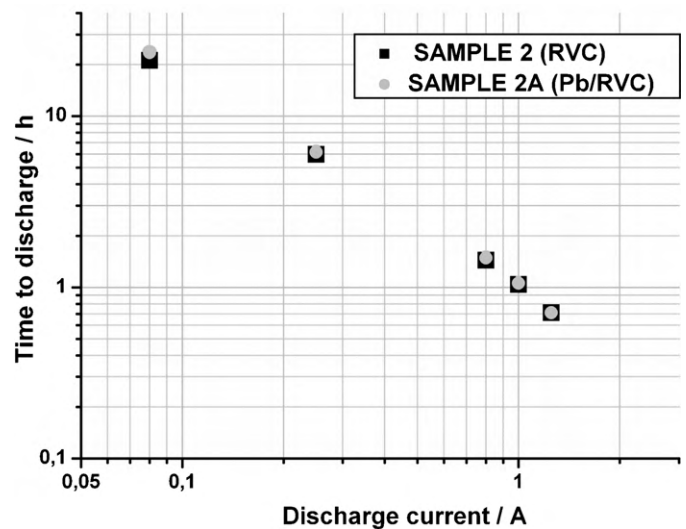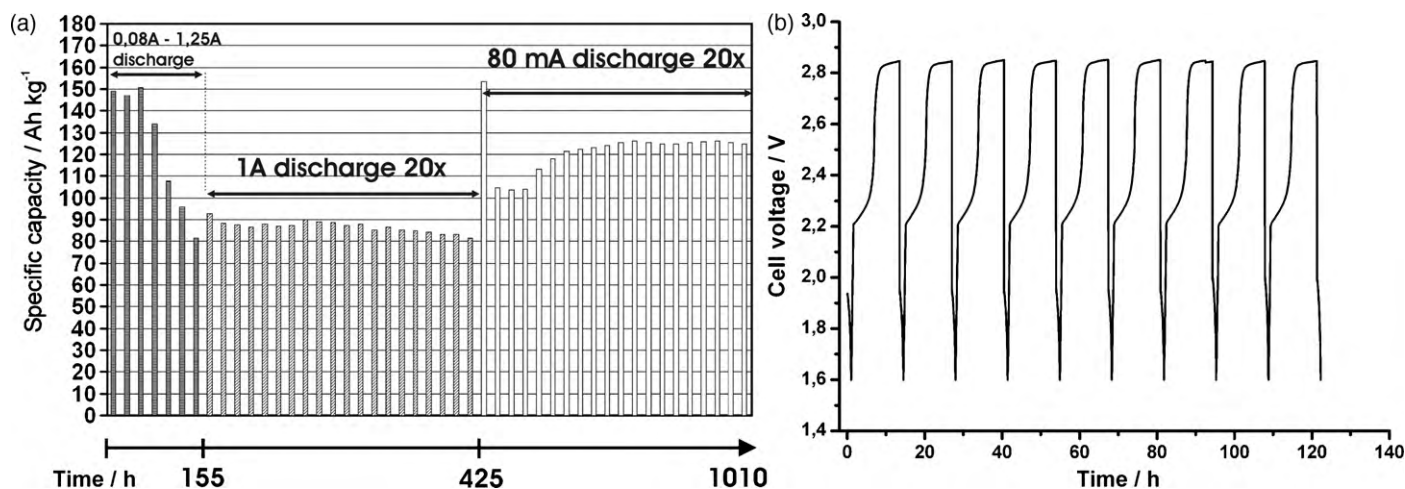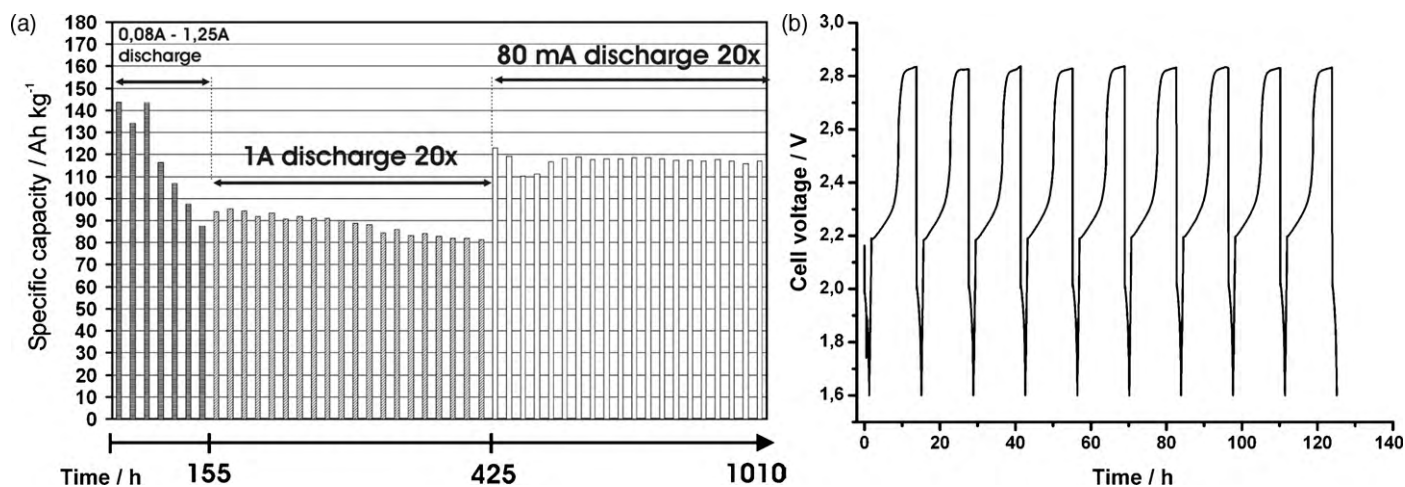

Fig. 5. Peukert dependences for lead-acid battery with Pb/RVC (sample 2) and bare RVC (sample 2A) based negative plate.

Fig. 6. (a) Battery capacity change during cyclic work of lead-acid battery with Pb/RVC-based negative plate. For the first three cycles discharge current was 0.08 A (the third was taken for electrical capacity estimation of the particular cell), the next four discharge cycles were taken for Peukert coefficient calculation (0.25, 0.80, 1.00 and 1.25 A). Next 40 cycles were taken with 1 A (20 cycles) and with 0.08 A (20 cycles) discharging currents. Charging 0.16 A, 12 h. (sample 1). (b) Cyclic characteristics of lead-acid battery with Pb/RVC-based negative plate for 1.00 A discharge current. Charging 0.16 A, 12 h (sample 1).

Fig. 7. (a) Battery capacity change during cyclic work of lead-acid battery with bare RVC-based negative plate. For the first three cycles discharge current was 0.08 A (the third was taken for electrical capacity estimation of the particular cell), the next four discharge cycles were taken for Peukert coefficient calculation (0.25, 0.80, 1.00 and 1.25 A). Next 40 cycles were taken with 1 A (20 cycles) and with 0.08 A (20 cycles) discharging currents. Charging 0.16 A, 12 h (sample 1A). (b) Cyclic characteristics of lead-acid battery with bare RVC-based negative plate for 1.00 A discharge current. Charging 0.16 A, 12 h (sample 1A).

At present we have results from new longer tests of both kinds of negative plates (with bare RVC and with lead covered RVC). It has to be noted that in the perspective of all tested plates in our experiments the electrochemical behavior of negative plates with Pb/RVC matrix show the tendency of better durability for higher current treatment in comparison to bare RVC [17]. This effect is due to the lead deposited on RVC.

4. Conclusions

RVC appears to be promising electrode material used in lead-acid battery. Both bare RVC and covered electrochemically with lead can be successfully employed as carriers and electrical collectors in negative plates of lead-acid battery. High specific capacity of active mass deposited on/in RVC carrier means that during charging–discharging process there is no interaction at interface between active mass and RVC or Pb/RVC. These results show also that RVC and Pb/RVC behave as good current collectors in the bulk

of active mass. Reasonable value of Peukert's coefficients show that negative plates constructed with RVC and Pb/RVC as carrier- and current-collector have good electrochemical behavior in wide range of discharging current (from 0.05 to 1 C). The application of RVC and Pb/RVC as the carrier- and current-collector lead to the increase of specific capacity of the negative plate which exceeds about 25% of specific capacity of the Pb alloy grid based plate (ca. 40% of Pb). Negative plate with RVC and Pb/RVC in continuous cyclic life tests for current between 0.05 and 1 C discharge currents shows also very promising behavior. Our batteries worked about 6 weeks and completed 47 full charge–discharge cycles. It should be noted that the RVC-based plates examined here were much thicker (3.5–4 mm) than regular Pb alloy grid based plates used in flooded or VRLA lead-acid batteries of different types (ca. between 0.8 and 3 mm). Production of thinner RVC plates will result in higher negative active material utilization which leads to subsequent raise of specific capacity of demonstrated hybrid lead-acid system.

Acknowledgements

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