Polish J. Chem., **78**, 1357–1370 (2004) **REVIEW ARTICLE**

Applications of Reticulated Vitreous Carbon (RVC$^{®}$) in the Electrochemical Power Sources*

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Reticulated Vitreous Carbon (RVC$^{®}$) is an open pore foam material composed solely of vitreous carbon *i.e.* glass-like carbon, but this material combines some properties of electron-conductive glass with some of those of normal industrial carbons. Over 200 papers have been published on different important electrochemical application of the RVC$^{®}$. The use of the RVC$^{®}$ electrodes modified with metals has benn proposed for the electrooxidation of impurities, optically transparent electrodes in thin layer constructions, removal and/or recovery of metal contaminations. This paper is a summary of recent literature on application of RVC$^{®}$ in electrochemical cells including our latest work. The use of RVC$^{®}$ in the construction of accumulators and batteries is discussed in detail showing the perspectives for wide application of this material in electrochemical power sources.

Key words: RVC, reticulated vitreous carbon, batteries, electrochemical power source, RVC modified with metals

1. Introduction

Reticulated Vitreous Carbon (RVC$^{®}$) has been developed for several non-electrochemical applications (*i.e.* high temperature insulation, acoustic control *etc*). This material is also useful for various electrochemical applications, particularly for electroanalytical purposes such as bath and flow analyses [1–4]. Over 200 papers have been published on different important electrochemical application of the RVC$^{®}$. The RVC$^{®}$ modified with metals have been proposed as electrodes for the electrooxidation of impurities, optically transparent electrodes in thin layer constructions, removal and/or recovery of metal contaminations. These electrochemical applications have been described widely in two reviews [3,4]. Both reviews have put little attention on using of RVC$^{®}$ as an electrode material in electrochemical cells.

In the last ten years, RVC$^{®}$ with its modifications has also been applied in cells and batteries constructions used on a smaller scale [4] than could be expected after its

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* Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

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application in analytical electrochemistry. RVC® has been only studied as material in electrochemical systems which are now very seldom or/and have some perspectives to be used as "real" sources of electrochemical energy. We found that this material can be used as matrix for active mass and current collector in many "classical" primary and secondary batteries. We have constructed the model of lead – acid accumulator and prototype of new type of zinc – manganese battery. The system of RVC®/Ni/NiOOH has been studied as complete cathode for secondary alkaline batteries *i.e.* Ni-Cd, Ni-Fe, Ni-MH and others. In another application, we have found that this material covered with thin platinum metals (especially with palladium) or their alloys can be adopted as power generating anode. The RVC®/Pd electrode [5] in co-operation with Jackowska's group has been adopted for preparation of RVC®/Pd/PANI (polyaniline) system, a new energy cumulating electrode.

This paper is a summary of recent literature on subject including our latest work. The use of RVC® in electrochemical power sources is discussed in detail showing the perspectives for wide application of this material in electrochemical powers sources.

2. Physical and Electrochemical Properties of Reticulated Vitreous Carbon (RVC®)

Reticulated vitreous carbon is an open pore foam material composed solely of vitreous carbon, *i.e.* glass-like carbon which combines some of the properties of electron-conductive glass with some of those of normal industrial carbons (Fig. 1).

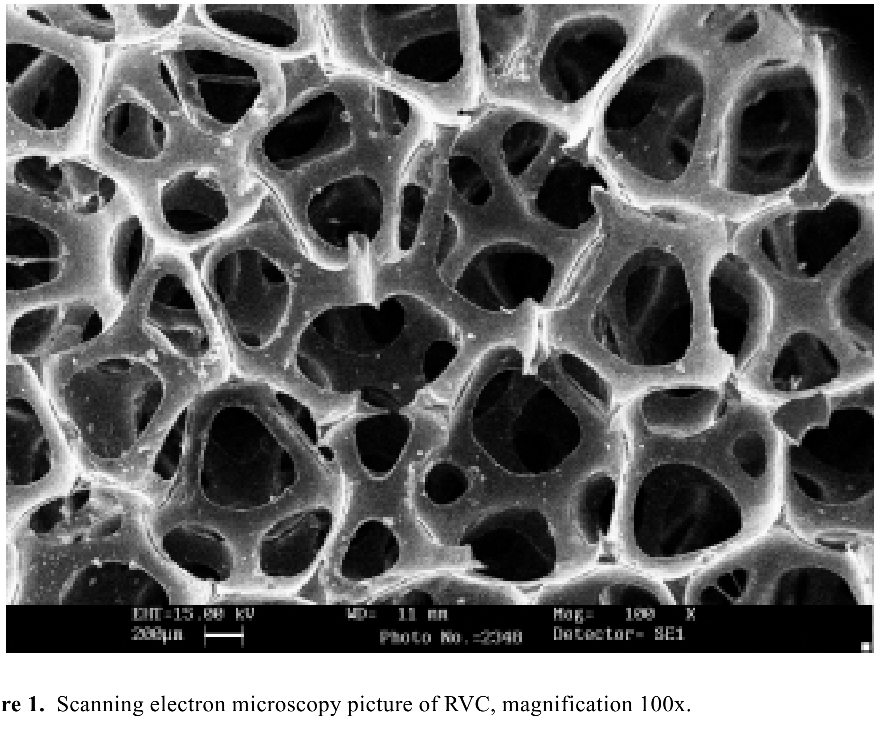

Figure 1. Scanning electron microscopy picture of RVC, magnification 100x.

RVC® is available in several porosity grades from 5 to 1400 pores per inch (ppi) *i.e.* the pores have the sizes from *ca.* 0.01 to 2.5 mm. Its porous, honeycomb structure provides low density, high surface area, unusual rigid geometry and a free void volume between 90% and 97% depending on the ppi grade. Although macroscopic area of reticulated vitreous carbon is high, its microscopic surface area remains low. It enables the capacitive current being low in comparison with other currents flowing through RVC® electrode. The high void volume results in low pressure drop in fluid flow, while mechanically continuous rigid structure makes the material highly electroconductive [1–4].

In spite of RVC®'s large surface area it does not support combustion after heating to bright incandescence in air followed by removal of the heat source. It is also highly resistant to intercalation by materials, which disintegrate graphite. RVC® is also inert to a wide range of very reactive acids, bases, and organic solvents. At high temperatures it will form carbides, but is inert to non-carbide forming metals and is not wetted by many molten metals. Heating in air at 315°C enhances its adsorption properties. Heating above 315°C in air atmosphere will result in significant oxidation of RVC® 's large surface area at rates that increase with increasing temperature [2]. In neutral gas atmosphere (*i.e.* argon) this material can be heated without surface changes at higher temperature.

Physical and chemical properties of RVC® and a wide potential range in which there are no faradaic processes on electrode surface (from 1.2 V to –1.0 V (*vs.* SCE) at pH 7 [4]) make this material very usable for the various electrochemical applications. In acidic solutions, RVC® can be well polarized in the range of potentials from 0.2 V to 1.4 V *vs.* SHE. Hydrogen and oxygen generation has been observed at 0.2 V and 1.4 V, respectively.

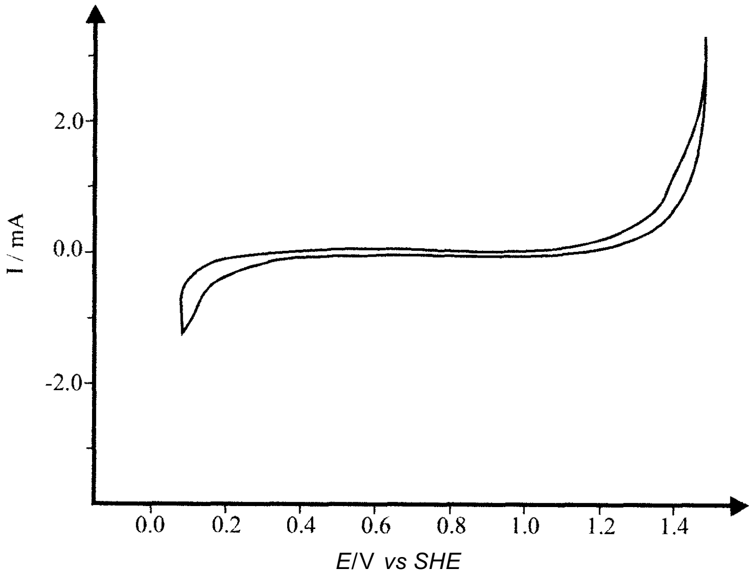

Figure 2. Cyclic voltammogram of the RVC electrode in 0.5 M H_2SO_4; 1st cycle; T = 298 K; v = 5 mV/s.

Structural features make RVC® ideal material for porous flow-through electrodes used in the removal of metal ions from waste solutions as well as in electrolytic processes, which yields are very often close to 100%. As already mentioned in the Introduction, there are lots of publications describing this branch of applications [3,4]. Flow-through RVC® electrodes may be successfully used in electroanalysis for the determination of electroactive species on the micromolar level [4]. There are also reports of using RVC® as an electrode material for electrochemical measurements in the batch systems [4]. RVC® is useful in the spectroelectrochemical measurements, as thin slice of RVC® is optically transparent [5]. There are applications of RVC® as a material for rotating disc electrodes as well [4]. Due to its high real surface, RVC® is also used in electrosynthesis [4], either as an electrode material or as a support for the catalyst layers [4].

Application of RVC® as a novel electrode material in the construction of electrochemical power sources may distinctly improve their characteristics. Main advantages of this material in the cell development are:

- ability of using it as an active mass carrier and current collector in the cell;
- large surface area allows good electric contact with electroactive species leads to increasing of current density of discharching, *i.e.* specific power density of cell;
- low density resulting in increasing of specific energy density of cell.

Almost 30 years since its development (in 1976), RVC® has been applied in not to many constructions of different types of the electrochemical power sources. Among them are primary and secondary batteries as well as fuel cells. This material has been applied in following electrochemical systems:

- microbial fuel cell;
- metal-halogen battery;
- polymer battery;
- zinc-manganese battery;
- lead-acid battery;
- alkaline batteries (cadmium or metal hydrides – nickel hydroxide batteries).

The research of our laboratory has been concerned on last five types of batteries [7–19].

3. Application of RVC® in Cells and Batteries

3.1. Microbial fuel cells. RVC® is also used in the research on microbial fuel cells. A microbial fuel cell is a device converting chemical energy into electrical energy, in which anodic potential is developed as a result of electron production during the oxidation of substrates by microorganisms [20–22]. Although direct transfer of electrons from microorganisms to electrode is possible, it is inefficient both in terms of the coulombic yield as of the rate of electron transfer. Thus, redox mediators are used [23–25]. RVC®, having a physical structure enabling microorganisms and mediators easy access to the surface, is used as anode material in microbial fuel cells. In the development of microbial fuel cell, important research has been performed by Roller *et al.* [23–25]. They conducted experiments in the fuel cell with a reticulated vitreous carbon anode and with platinum foil cathode. 0.1 M phosphate buffer, pH 7.0, was used as the anolyte and the catholyte was 0.2 M potassium ferricyanide in 0.1 M potassium phosphate buffer. In the anodic compartment of the cell fuel is oxidized by microorganisms and electrons are produced which, in turn, are captured by the oxidized mediator and transferred to the anode. At the anode, the mediator is reoxidized. In the cathodic compartment, ferricyanide is reduced to ferrocyanide at platinum [26]. A cation-permeable ion exchange membrane separated electrode compartments. The authors tested variety of microorganisms as well as mediators. Among them, thionine as a mediator, *Proteus vulgaris* as a microorganism and a glucose as a substrate was chosen as the efficient system for obtaining coulombic yields of 32–62% in a phosphate buffer at pH 7 (organism concentration was 1.5 mg (dry wt) ml^{-1}).

Kim *et al.* developed a prototype microbial fuel cell using *P. vulgaris* with $RVC^{®}$ anode and Pt/ferricyanide system as a cathode [26]. Electrode compartments were separated by Nafion® membrane. They found thionine as an effective redox mediator. The fuel cell performance was maximum at 37°C, the optimum temperature for *Proteus vulgaris*, and dependent on the mediator concentration. Among the tested carbon sources, glucose showed coulombic efficiency of 29% while galactose showed 56% efficiency.

The same authors studied behaviors of redox mediators within the hydrophobic layers and their influence on the microbial fuel cell operation efficiency [27]. They compared capability of thionine and safranine O for penetration of the lipid layer. Although both mediators easily penetrated the lipid layer, only thionine could pass through the layer while gradual accumulation of safranine O within the layer was observed. This resulted in very low current output in the fuel cell with safranine O as mediator in comparison with the fuel cell with thionine as a mediator. The microorganisms used in the fuel cell were *Proteus vulgaris* and *Escherichia coli*.

Wilkinson presented recently food powered mobile robot using stack of microbial fuel cells with 100 ppi $RVC^{®}$ as an electrode material [28,29].

3.2. Metal – halogen cells. The zinc – bromine system has a much lower energy density than zinc – chlorine, but the comparative ease of handling bromine and absence of refrigeration requirements make it an attractive alternative. Due to this behavior the zinc-bromine battery appears to be potentially attractive for energy storage. Although it has been studied for a long time, self-discharge phenomena associated with the high solubility of Br_2 in aqueous electrolytes, and dendritic zinc deposition have hampered its development. One of possible ways to overcome the former difficulty is to use complexing agent for Br_2. The second difficulty can be settled by determining the conditions for obtaining uniform, Zn plating.

Mastragostino and Valcher [30] examined the possibility of using a polymeric salt, poly(diallyldimethylammonium bromide) (PBr) as bromine complexing agent in the rechargeable Zn-Br_2 battery. They used reticulated vitreous as electrode material. $RVC^{®}$ with different porosity (100 ppi ($RVC^{®}$-S100) and 60 ppi ($RVC^{®}$-S60)) was used in order to overcome the difficulty related to the low current density and also

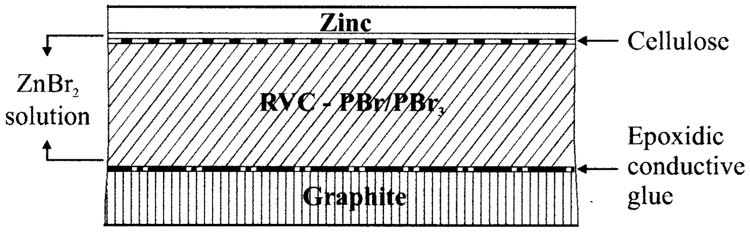

Figure 3. Scheme of Zn-Br_2 rechargeable cell [30].

to retain the solid complex of bromine generated during the charging stage. The scheme of this battery was already shown in Fig. 3.

Mastragostino and Valcher [30] also examined the influence of RVC® layer thickness, porosity grade, and also amount of PBr on the performance of electrodes. The best results were obtained with RVC® porosity grade of 100 ppi. The behavior of positive electrode was studied with the increase of the amount of PBr at constant RVC® thickness as well as decrease of RVC® thickness at constant PBr amount. Both modifications impaired the electrode performance. A good coulomb efficiency at reasonably high values of current density for the Zn-Br_2 battery with the RVC®/PBr electrode was obtained. A self-discharge rate was 0.01 A dm^{-2} at 298 K. The behavior of the system strongly depends on the technique used to introduce the polymer salt into the pores of the electrode.

The RVC® material has also been applied in Zn-Br_2 battery as the carrier of active mass of negative electrode. Iacovangelo and Will [31] studied deposition of zinc on reticulated vitreous carbon. They determined conditions, under which uniform Zn plating without dendrite formation could be obtained. Zinc was deposited on RVC® foams with circulating electrolyte. RVC® carrier with Zn was cemented to graphite current collector plates with a conductive adhesive. For quantitative analysis of Zn deposition within RVC®, X-ray absorption coupled with densitometry and microscopy was applied. Zn deposits are more uniform at high electrolyte flow, high pore length/pore diameter ratio, and thicker foams. Within the range of parameters studied, they obtained optimal results with 2 mm thick 100 ppi RVC® foams with electrolyte flow rates corresponding to Reynolds numbers close to 500. Addition of an organic dendrite inhibitor-solubilizer combination to the electrolyte resulted in obtaining dendrite-free Zn deposits when plating at charge densities up to 200 mA h cm^{-2}.

3.3. Zinc-manganese (carbon) batteries. The zinc-manganese dioxide system, firstly constructed by Leclanché, is known as one of oldest commercial primary battery. It is still considered as the most popular battery (35% of world production) system used in the construction of zinc-carbon dry cells. This system was constantly improved from the beginning. Till 60's of the last century in every twenty years the electrical capacity increase was 100%. From 80's it was found that the capacity of zinc-manganese reached theoretical value. In our laboratory the RVC® was applied in this cell as the current collector and cathodic mass carrier. This operation allowed us to increase free volume of cells available to cathodic mixture *i.e.* MnO_2 + acetylene black. As electrolyte NH_4Cl with $ZnCl_2$ solution was used *i.e.* the component used in the Leclanché batteries of lowest efficiency. The differences between our and commercial batteries used now is shown in Fig. 4.

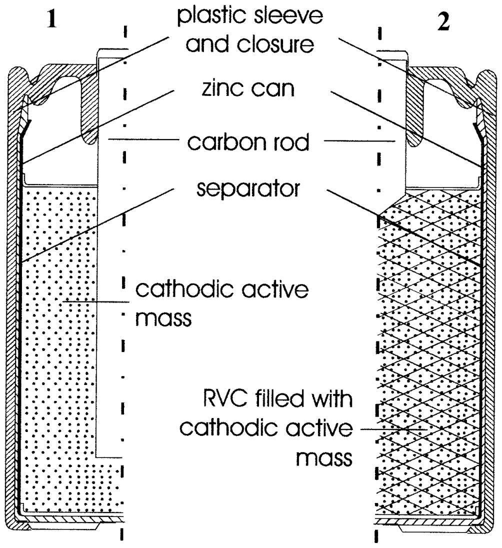

Figure 4. Cross section of the classical (1) and modified (2) primary zinc-carbon cell.

The discharge mechanism of the zinc-carbon cell is complex and the insoluble products of the electrode reactions such as ammonia complexes and oxychloride species are formed. Precipitation of insoluble compounds increases cell resistance. To avoid this problem Rogulski and Czerwiński [7–10] proposed a new construction of the cell, in which the carbon (graphite) rod, usually used in the cell for the cathodic current collector has been substituted in demonstrated construction by RVC® (Fig. 4). In their cathode construction RVC® is used as the current collector and the carrier for the cathodic active mass (mixture of MnO_2 and acetylene black). In this situation each pore acts as a semi-separate cell. If an unwanted reaction takes place in this semi-cell *e.g.* precipitation of insoluble compounds, only this small part of the cathode area is switched off. For this reason the proposed modification of the cathode construction should lead to better parameters of operation. Due to this construction changes it was possible to decrease the concentration of acetylene black in the cathodic mass by *ca.* 7% (from 10 to 3%). It leads to the growth of MnO_2 quantity in the cell, *i.e.* the increase of cell capacity. The capacity of our cell in comparison with commercial cell, where $ZnCl_2$ solution have been used as electrolyte are shown in Fig. 5. This kind of cell with zinc chloride solution are called Heavy Duty batteries as they have higher capacity than classical Leclanché batteries with NH_4Cl solution.

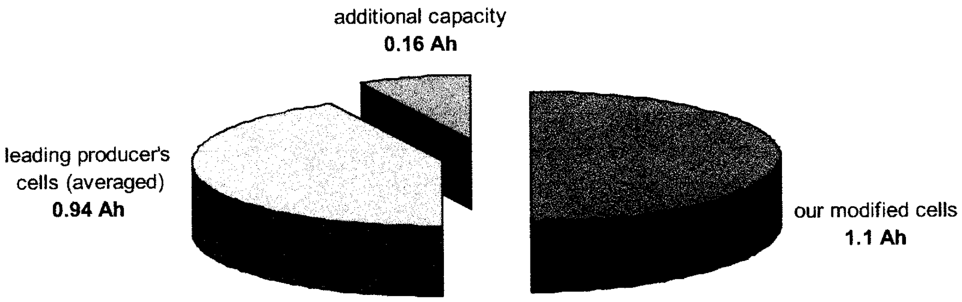

Figure 5. Comparison of electrical capacity of a classical and the modified zinc-carbon cell.

The results obtained for various test modes have shown the discharge times of new zinc-carbon cell to be longer than these of commercially available batteries. The comparison of our and commercial cells discharging are demonstrated in Fig. 6.

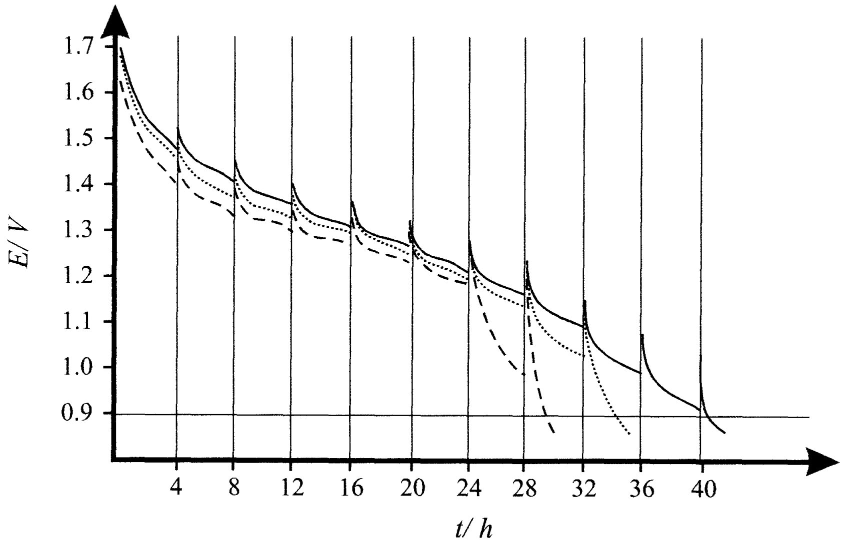

Figure 6. The intermittent discharge curves of the modified (solid line) and classical (dashed and dotted lines) obtained in test mode simulated work of portable recivers (43 Ω).

Additional benefits of this new construction were:

- increase of electrical capacity;
- rise of discharge current;
- improvement of voltage stability during discharge.

The element that has main influence on the total cost of modified zinc-carbon cell production is reticulated vitreous carbon. From a rough economic calculation we found that the introduction of RVC to zinc – carbon cells should rise the battery manufacturing cost by *ca.* 0.005–0.01 $ per unit relative to classical GP Leclanché cells based on the ammonia chloride electrolyte.

At this moment our group has advanced works with RVC® application in new acidic rechargeable zinc – manganese batteries [11].

3.4. Batteries involving polyaniline (PANI). Polyaniline (PANI) is a conducting polymer known as an electronic as well as an ionic conductor, therefore it would be advantageous to use it as a positive electrode material in battery design [32]. Among other conducting polymers, polyaniline (PANI) is a promising one since it has the following advantages:

- it can be synthesized in either chemical or electrochemical manner;
- its preparation is very simple;
- it is resistant for aerial oxidation as well as for moisture;
- gives reversible electrochemical response.

Non-aqueous as well as aqueous electrolytes have been used in polyaniline-based batteries. As a negative electrode material, typically Li or Li-Al was used in non-aqueous electrolytes, while Zn was used in aqueous ones. Tsutsumi *et al.* presented a model of a secondary cell which consisted of Li/$LiClO_4$-propylene carbonate/PANI-poly(*p*-styrenesulfonic acid)-RVC® [33,34]. The PANI-poly(*p*-styrenesulfonic acid)-RVC® electrode was prepared by dipping a RVC® electrode into the PANI-*p*-styrenesulfonic acid composite/solvent mixture and heating for 5 h at 100°C. The cell showed about 60% coulombic efficiency under high current density cycling conditions (3.8 A g^{-1} of modified RVC®/PANI-poly(*p*-styrenesulfonic acid electrode) and the value was constant over 30 cycles. The capacity of the cell gradually decreased with continuous cycling. After the continuous charge-discharge cycling, the PANI-poly(*p*-styrenesulfonic acid) composite peeled from the RVC® electrode. Optimization of the current density and the amount of modified PANI-poly(*p*-styrenesulfonic acid) composite on the RVC® electrode is necessary for further application of PANI-poly(*p*-styrenesulfonic acid) composites used in a rechargeable lithium battery.

Mirmohseni and Solhjo demonstrated aqueous polyaniline rechargeable battery of the type Zn/$ZnCl_2$, NH_4Cl/PANI-RVC® [35]. Polyaniline-RVC® electrode was prepared by the electropolymerization in a three electrode system involving a working electrode of a high-porosity RVC®, a counter electrode made from another RVC® and Ag/AgCl reference electrode. A constant potential of 0.7 V *vs.* Ag/AgCl was employed in a solution containing 2 M aniline in 1 M HCl. Charging process of the battery was conducted galvanostatically. The best current density for charging was found to be 0.2 mA cm^{-2}. The discharge curve was obtained for the battery under two constant loads at 2.5 and 5 kΩ and the amount of electricity obtained was 56 and 53 C, respectively. The open circuit potential (OCP) of the battery was approximately 1.2 V. The discharge cut-off potential was about 0.4 V. The battery had an output capacity of 121 mA h g^{-1} (based on the weight of dry polymer). The coulombic efficiency was in the range between 75% and 100%. Self-discharge rate was less than 1% per day and the battery showed a good cycle ability.

Frydrychewicz *et al.* [5] has prepared electrode storage obtained by electrolysis of Pd particles in/on PANI electrodeposited on RVC®. It was proposed as a material suitable for hydrogen storage. This Pd/PANI/ RVC® system seems to be applicable as negative electrode in rechargeable cells.

3.5. Lead-acid batteries. Despite the fact, that it was invented over 140 years ago, the lead-acid battery still remains one of the most widely used secondary power sources. During this period of time, construction of lead-acid battery has changed, but still the main disadvantage of classic lead-acid battery is low energy density in relation to mass of electrode. This is a result of two factors [36]:

- the use of lead as the current collector material and the internal connectors;
- poor utilization of the active materials.

Pavlov introduced γ parameter, reflecting the ratio of positive active mass to collector surface area [37]. This parameter ranges for typical lead-acid batteries between 1.6 and 1.8 for tubular and 2–2.5 for book-mould SLI (starting-lighting-ignition) plates, respectively. In order to increase the utilization efficiency of the positive active mass, the latest trend is to design plates with low γ factors. To achieve this, attempts are made to replace lead current collectors used in these batteries with other light-weight electroconducting material. Carbon current collectors seem to be very promising, (*e.g.* [36,38]).

Our results [12–16] have shown that Pb, as well as PbO_2, can be deposited on reticulated vitreous carbon. Both electrodes exhibit almost identical electrochemical behavior to pure metallic lead and PbO_2 deposited on lead carrier. By the comparison with a system in which RVC® was coated with a layer of platinum, and subsequently with lead (or lead oxide), we found that RVC® matrix has no significant influence on the electrochemical characteristics of the system. Since RVC® constitutes as a very

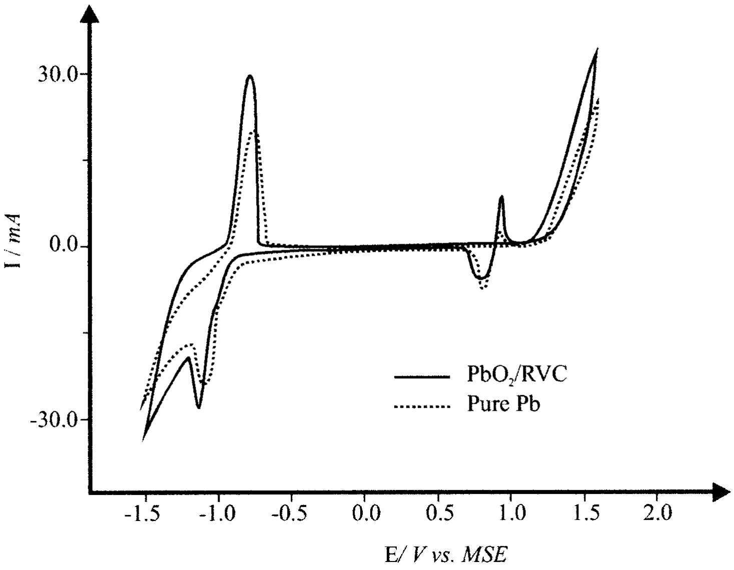

Figure 7. Cyclic voltammograms of the PbO_2/RVC and Pb electrodes in 0.5 M H_2SO_4; 1st cycle; T = 298 K; v = 1 mV/s.

good matrix for depositing lead and PbO_2 onto its surface, RVC® could be a good material for current collectors for lead-acid batteries. The Pb/RVC® and PbO_2/Pb/RVC® systems has been proposed as good carries for active electrode mass which can be used in lead-acid batteries. In Fig. 7 are shown the cyclic voltammograms obtained for pure lead and lead dioxide deposited on RVC®. The electrochemical behavior of both electrodes proved that is no influence of RVC® matrix on deposited lead.

We have proposed that these systems can be used in new construction of lead – acid batteries. The battery with those electrode matrix-carriers where RVC® is covered with a thin layer of lead or lead with lead dioxide [Figs. 8a and 8b] has been patented described in three patents [12,15,16].

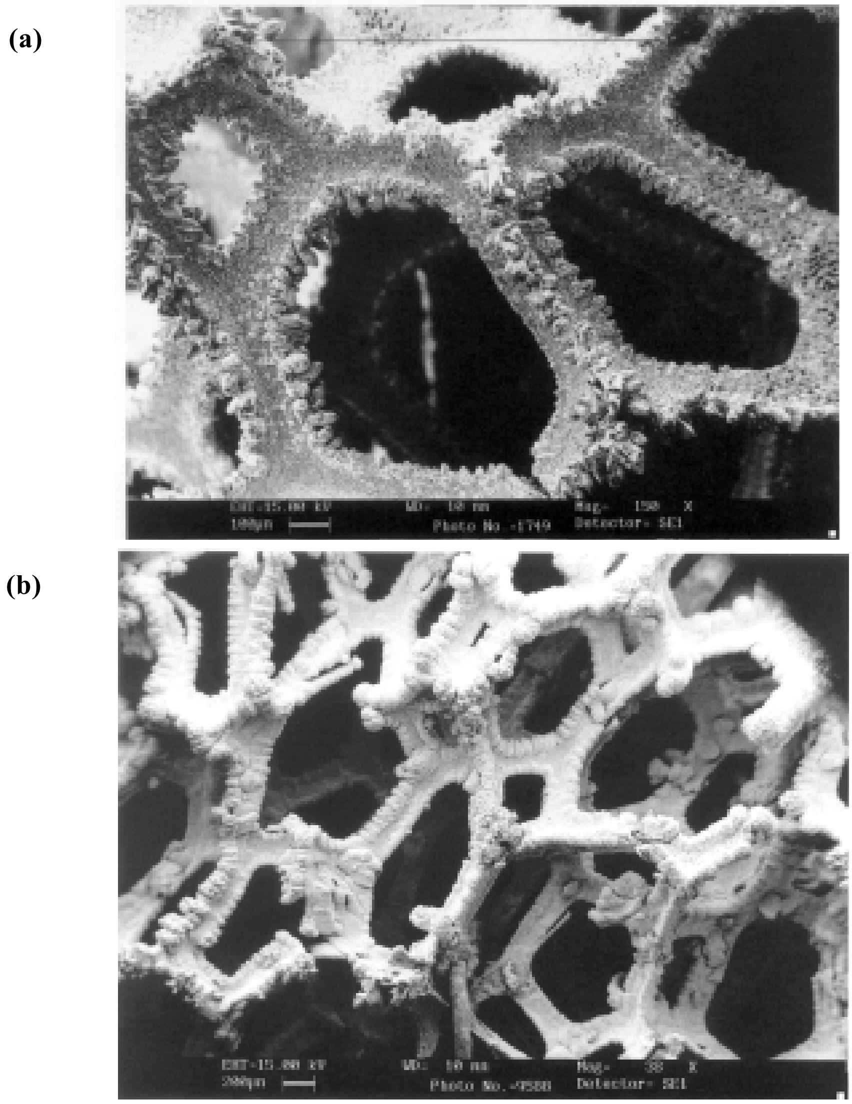

Figure 8. Scanning electron microscopy pictures of Pb/RVC (a) and PbO_2/RVC (b) electrodes.

Gyenge *et al*. [39–41] has adapted the Czerwiński's idea (presented in a 1995 patent [41]) and demonstrated current collectors made of RVC® with a γ factor of about 0.1. They galvanostatically plated RVC® slabs with a Pb-Sn (1 wt.%) alloy, using a fluoroborate bath. A coating thickness for the positive collector was typically 200–300 μm, and for the negative collector 80–120 μm. Flooded, 2V single-cell lead-acid battery completed 500 cycles corresponding to over 1500 h of continuous operation, involving discharges at 63 A per kg of positive active mass, 0.75 h rate and nominal positive active mass utilization efficiency of 21%. These results have been showed in a patent [41].

3.6. Batteries with NiOOH cathode. NiOOH electrode has been widely used in various types of rechargeable alkaline batteries as a cathode material. One of reasons for conducting the studies on the development of nickel batteries is the necessity for the reduction of the amount of dangerous and polluting materials used in these batteries and accumulators.

Our group with cooperation with Central Laboratory of Cells and Batteries from Poznań [17–19] investigated the electrochemical behavior of nickel electrodeposited on RVC® as a possible cathode material in rechargeable alkaline batteries *i.e.* nickel-cadmium and nickel-metal hydride accumulators. In Fig. 9 shown nickel deposit on RVC®. RVC® is covered regularly without spots from matrix. Electrochemical treatment of obtained Ni/RVC® electrodes confirmed expected good adhesion of nickel to carbon background [19].

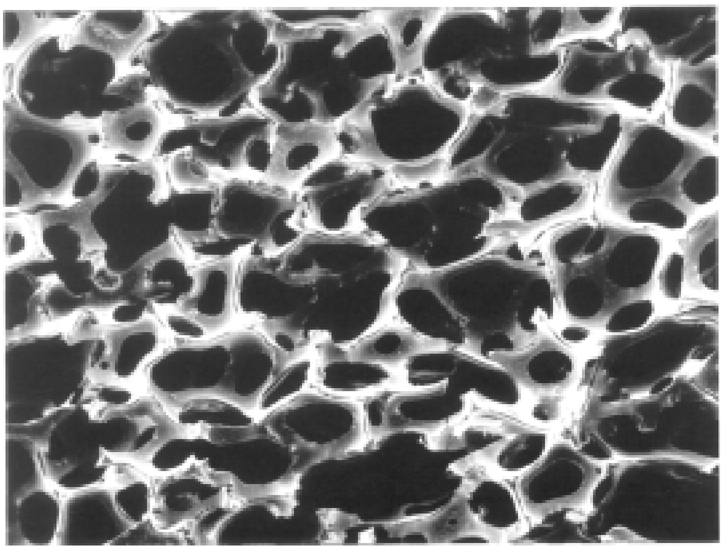

Figure 9. Scanning electron microscopy picture of Ni/RVC electrode, magnification 100x.

We found that Ni/RVC® system displays identical electrochemical behavior to solid pure nickel and both sintered nickel and nickel foam which are widely used as a carrier for nickel hydroxides – the material of positive electrodes. In particular, the shapes of charge-discharge curves for Ni/RVC®-$Ni(OH)_2$/NiOOH and sintered

Ni-Ni$(OH)_2$/NiOOH systems were very similar. The results of energy capacity calculation led them to the conclusion, that the batteries supplied with Ni/RVC®-NiOOH electrodes, when compared with sintered Ni-NiOOH electrodes, have much better weight specific energy (approximately two times).

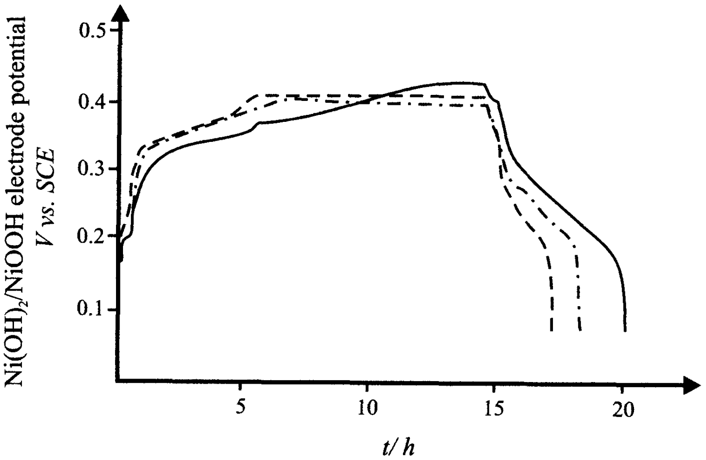

Figure 10. Charging-discharging curves of Ni$(OH)_2$/NiOOH electrodes deposited on RVC (dashed-dotted line), sintered porous nickel (dashed line) and foam of nickel (solid line) in 6 M KOH. The charging current was held at current 0.1 C per 14 hours. Discharging was held at current rate 0.2 C and finished at potential 0.08 V.

We concluded that Ni/RVC® system could be a good matrix for Ni$(OH)_2$/NiOOH electrodes for the future studies with the focus on a possibility of using these electrodes in the rechargeable batteries (*e.g.*, Ni-Cd, Ni-Fe, Ni-MH).

4. Summary

Many advantages of reticulated vitreous carbon (RVC®) decided that this material has been found for application in various branches of electrochemistry. Till now RVC® have not been found in so many application in battery field as it was done in the other electrochemistry branches especially in electroanalytical chemistry. In this paper it has been showed that RVC® or modified RVC® with metals used as a new electrode material pick up the performance of batteries in comparison to classical cells which now very often have reached theoretically limits. RVC® can be also applied in new type of electrochemical power sources *i.e.* modified RVC® in electrochemical supercapacitors.

RVC® has a future in the application in many kinds of electrochemical power sources as an electrode material and/or current collector with the matrix and carrier function in new types of cells.

Acknowledgments

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