

Electrochemical behavior of lead dioxide deposited on reticulated vitreous carbon (RVC)

Andrzej Czerwiński *, Małgorzata Żelazowska

Department of Chemistry, Warsaw University, Żwirki i Wigury 101, 02-089 Warsaw, Poland

Abstract

The electrochemical performance of lead dioxide deposited on reticulated vitreous carbon (RVC) has been investigated in basic and acidic solutions (0.1 M NaOH, 0.1 M Na₂B₄O₇ and 0.5 M H₂SO₄). For comparison, pure lead and lead dioxide deposited on platinized RVC (Pt/RVC) were also included in the study. Our results indicate that the behavior of RVC covered with lead dioxide (without platinum) resembles that of lead dioxide generated electrochemically on metallic lead.

Keywords: Reticulated vitreous carbon; Lead; Lead dioxide; Electrodes

1. Introduction

Reticulated vitreous carbon (RVC) [1] has been widely applied as an electrode material [2]. RVC is characterized by a very high area: volume ratio and by an open pore structure with a relatively large volume (90–97% depending on the respective porosity grade). Initially RVC was not designed for electrochemistry. (It was designed as acoustic isolator for example.) However, it was quickly evident that RVC could be a very good electrode material suitable for flow-through cells due to its low resistance to fluid flow [3–7] and excellent for use in optically transparent electrodes (OTE) [8–14]. RVC has mostly been applied in the electroanalysis [3–34]. Using RVC covered with a thin layer of metal it was possible to prepare high-surface-area metallic electrodes with the minimum consumption of precious and expensive metals. RVC covered with a thin layer of platinum, rhodium, platinum–rhodium alloy [17,18], ruthenium [19] or palladium [20,21] shows a performance analogous to the electrodeposited metal itself that is not affected by a carbon background. Such electrodes connected with fuel cells, have been applied to study the sorption of methanol oxidation products on platinum group metals [17–19]. An optically transparent thin layer electrode (OTTLE) has been prepared by vacuum or by electrodeposition of a thin gold film on RVC [11]. RVC provides very large surface areas which could also be easily plated with mercury [22–27]. Mercury-coated RVC electrodes have been used for the determination of trace metals. RVC was employed as an electrode for decontamination

of Pb(II) cations and other heavy metals from solutions [31,34,35]. PbO₂ electrodeposited on RVC was used by Tissot and Fragniere [36] for the oxidation of cyanide from aqueous solutions. We also demonstrated that such a good electric conductor as RVC can be easily modified (covered) with lead [37]. We found previously [37] that RVC is a very good material substrate for depositing lead and the electrochemical behavior of the RVC substrate covered with lead is almost identical to the behavior of metallic (pure) lead in basic and acidic solutions.

In this report, we describe the electrochemical performance of RVC substrates covered with PbO₂ investigated in various solutions (sodium hydroxide, sodium borate or sulfuric acid). The resulting electrodes show virtually identical electrochemical performances to solid lead with deposited PbO₂. In order to verify the matrix influence on deposited PbO₂, we have also studied RVC modified with platinum and subsequently covered with PbO₂. Like in a previous paper all results are compared with data obtained for pure lead (on which during cyclic polarization were generated lead oxides) and with our results [37] on Pb/RVC and Pb/Pt/RVC in basic and acidic solutions earlier reported [37].

These results might be of practical importance since RVC covered with lead and PbO₂ offer a potential as a new electrode material in electrical energy sources.

2. Experimental

2.1. Apparatus

Current–potential curves were recorded using potentiostat/galvanostat PGS 201T TACUSSEL controlled by an

* Corresponding author.

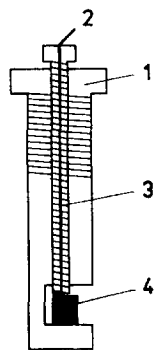


Fig. 1. Schematic diagram of the electrode holder assembly: (1) Teflon rod; (2) platinum contact; (3) Teflon screw, and (4) RVC sample.

IBM compatible computer 486 DX-40. The curves were recorded with a HP DJ 510 printer. Micrographs of the modified RVC surfaces were obtained with a JEOL JFM-S1 scanning electron microscope (SEM).

2.2. Electrode holder construction

The holder for electrochemical measurements is shown in Fig. 1. The electrode holder assembly resembles that constructed previously to study insoluble conducting polymers [38]. To provide a good electrical contact a platinum wire was inserted into a small hole which was drilled along the length of the Teflon rod, $d = 20$ mm. The RVC material was inserted into a slot at the bottom of the electrode holder, and it contacted the platinum wire by applying pressure on the Teflon screw. The area of the platinum wire which was in contact with RVC was negligible in comparison with the RVC material area. To avoid any photoelectric effect in the experiments [39], the cell was kept in a dark compartment.

2.3. Chemicals and materials

All chemicals were of a high grade quality. They were used without further purification. Cyclic voltammograms of metallic lead and PbO_2/RVC electrodes were recorded in 0.1 M NaOH, 0.1 M $\text{Na}_2\text{B}_4\text{O}_7$ and 0.5 M H_2SO_4 solutions (Ciech, Poland). The solutions were prepared from highly de-ionized water (Millipore) and de-aerated with argon. The RVC, with a porosity of 45 ppi, was from ERG—Materials and Aerospace Corporation. According to the manufacturer's specifications, the real surface area of RVC was about $30 \text{ cm}^2/\text{cm}^3$. The used volume of RVC samples in experiments was about $0.25 \text{ cm}^3 (\pm 20\%)$.

2.4. Electrodes

A silver chloride electrode (Mineral, Poland) and a platinum black foil (4 cm^2 of geometric area) were used as the reference and auxiliary electrodes, respectively. All potentials in the text and figures are referred to a saturated calomel electrode reference electrode (SCE). The PbO_2/RVC and $\text{PbO}_2/\text{Pt}/\text{RVC}$ systems served as the working electrodes. To

verify the results obtained with PbO_2/RVC and $\text{PbO}_2/\text{Pt}/\text{RVC}$, bars of pure lead (99.9%, Ciech, Poland) were used as the lead standards for comparison. The geometric area of lead bars was close to calculated surface of RVC, the latter being based on the manufacturer's specifications. The voltammograms of the lead electrode were taken under the same conditions as those of PbO_2/RVC and with use of the same holder shown in Fig. 1.

2.5. Preparation of PbO_2 electrode

Anodic plating of PbO_2 on RVC was accomplished from acetate or nitrate solutions [40–43]. We found that PbO_2 deposited from acetate solution has mainly the α -rhombohedral structure. From nitrate solution we obtained mainly the β -tetragonal structure (≈ 70 – 80%). The structure of PbO_2 deposits was investigated by X-ray diffraction using Philips Diffractometer ($\text{Cu K}\alpha$ radiation) in Central Laboratory of Batteries and Cells (CLAiO) in Poznań, Poland.

The dependence of the structure of PbO_2 on deposition solution was in agreement with data in Ref. [43]. In this paper we refer to PbO_2 electrodes obtained from nitrate solutions only. The current, recorded during electrolysis at 60°C , was ≈ 1.5 – $2.0 \text{ mA}/\text{cm}^2$. Time of the electrolysis was 20–30 min.

A typical SEM micrograph of PbO_2 which was deposited from a nitrate solution is shown in Fig. 2. Electrodes of PbO_2 deposited on the RVC substrate, which were previously covered with platinum, were included to evaluate any matrix effects on the deposited PbO_2 . The procedure for platinum-deposition on RVC was as previously described in detail in Refs. [17,37]. The SEM micrograph of the RVC surface covered with platinum was showed in Ref. [37]. We dem-



Fig. 2. Scanning electron microscope picture ($\times 100$) obtained for PbO_2 deposited on RVC from a nitrate solution.

onstrated earlier [17] that platinum electrodeposited on RVC shows voltammetric characteristics analogous to that of pure platinum.

3. Results and discussion

3.1. 0.1 M NaOH

Fig. 3 shows the cyclic voltammetric performance of the PbO_2/RVC electrode in 0.1 M NaOH. The voltammograms were recorded in the potential region between -1.5 and 0.7 V versus SCE. In the first cathodic scan for PbO_2/RVC we started from an anodic potential of $+0.16$ V at which neither oxidation nor reduction currents were observed.

As we showed before [37,17] the background currents originating from pure RVC and the contact platinum wire are negligible. During electrodeposition, PbO_2 is deposited not only on the RVC but also on the platinum wire. The results are compared with data obtained for pure lead. The obtained cyclic voltammograms are very similar to those presented in Fig. 4, i.e. to the voltammograms obtained for the pure-lead metal electrode where the respective cyclic voltammograms at a very low scan rate (0.5 mV s^{-1}) have been recorded starting from a negative potential (-1.50 V versus SCE).

The results presented in Figs. 3 and 4 show that there are no significant differences in the voltammetric performance

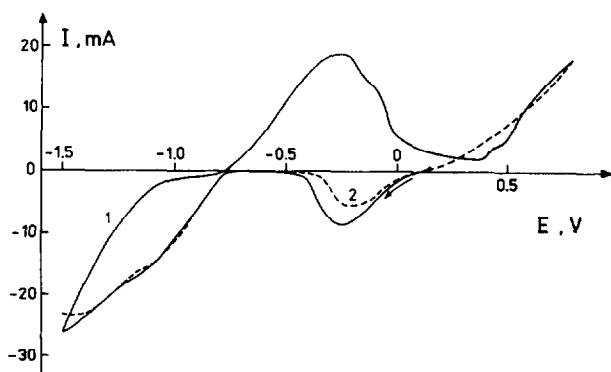


Fig. 3. The cyclic voltammograms of (a) PbO_2/RVC electrode in 0.1 M NaOH solution. Sweep rate: 0.5 mV s^{-1} . (—) first, and (---) next sweep.

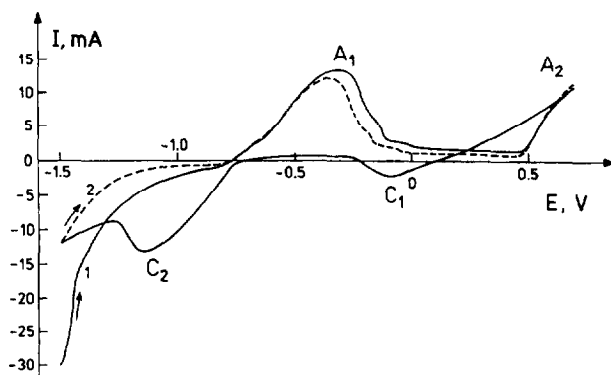


Fig. 4. Cyclic voltammograms of a lead electrode in 0.1 M NaOH. Sweep rate: 0.5 mV s^{-1} . (—) first, and (---) next sweep.

between metallic lead (which surface is oxidized to PbO_2 during anodic polarization) and PbO_2/RVC electrodes, i.e. the electrodes PbO_2/RVC and pure-metallic lead show the same behavior in the 0.1 M NaOH solution. In the cyclic voltammograms of lead and PbO_2/RVC , two cathodic peaks (denoted as C_2 and C_1 in Fig. 4) and two anodic peaks (marked as A_1 and A_2 in Fig. 4) have been observed in the first and subsequent scans. Only small differences between the potentials of the peaks has been observed for lead and PbO_2/RVC electrodes included in the study. It seems that the effects of RVC matrix on lead-surface processes in NaOH solution are rather small.

Cyclic voltammograms characteristic of PbO_2 deposited on Pt/RVC ($\text{PbO}_2/\text{Pt/RVC}$) are shown in Fig. 5. These voltammograms were recorded in the potential region between -1.5 and 0.7 V versus SCE.

A different situation is observed during cycling polarization of PbO_2 deposited on Pt/RVC. The voltammogram for PbO_2 deposited on Pt/RVC matrix looks different from that for PbO_2/RVC . After a second sweep, the currents responsible for surface reactions practically disappeared. At the same time, flaking of the PbO_2 layer from Pt/RVC matrix was observed.

Centeno et al. [44], who studied PbO_2 powder admixed with carbon paste, observed two cathodic and two anodic peaks in the electrochemical performance of PbO_2 in the second scan and the following cathodic scans. In our experiments, potentials of the cathodic peaks are comparable with those reported by Centeno et al. [44]. However, some differences exist in the potentials of peaks. We did not observe another (third) cathodic peak, in contrast to that observed (at -0.35 V) by Centeno et al. [44] in first cyclic sweep. We did not observe this peak neither during the study of lead deposited on RVC [37]. It has to be noted that this peak is not visible in voltammograms showed by Birss and Shevalier [45] who studied lead oxides in NaOH. The shape and potentials of the cathodic peaks obtained by Briss and Shevalier [45] differ from our data probably due to the effect of a higher NaOH concentration (1 M NaOH) which leads to a faster dissolution of lead oxides. The differences between our findings and those of Centeno et al. [44] could have origi-

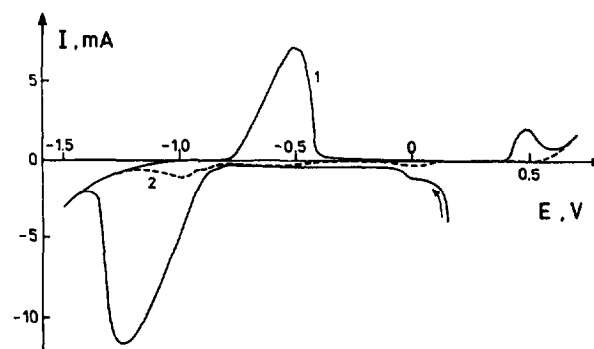


Fig. 5. The cyclic voltammograms of $\text{PbO}_2/\text{Pt/RVC}$ electrode in 0.1 M NaOH solution. Sweep rate: 0.5 mV s^{-1} . (—) first, and (---) next sweep.

nated from distinct morphologies of PbO_2 electrodes. In a previous paper [37] we also compared our experiments with lead deposited on RVC and Pt/RVC to the results obtained by Centeno et al. [44]. The effect of sulfate cations in an alkaline solution on the shape of PbO_2 cyclic voltammograms was observed by Veluchamy et al. [46] in their studies of photoelectric properties of PbO_2 . In agreement with our findings, no other cathodic peak was observed either in the voltammograms presented in Ref. [46]. Only in the case of the RVC matrix is the electrochemical behavior of deposited PbO_2 similar to the behavior of lead reported in the literature. In view of data in Refs. [44,45,47] the peaks A_1 and A_2 for lead and PbO_2 represent two oxidation steps of surface lead to Pb(II) and Pb(IV) , respectively. Peaks C_1 and C_2 , represent the electrochemical reduction of Pb(IV) and Pb(II) to Pb(0) .

It has to be noted that during the study of the behavior of lead deposited on RVC and Pt/RVC there is no fundamental difference between the electrochemical behavior between pure-metallic lead and those electrodes in the basic solution of 0.1 M NaOH [37]. The thus obtained voltammograms for Pb/RVC and Pb/Pt/RVC [37] were similar in shape to those for PbO_2 /RVC.

3.2. Borate solution

The solubility of the lead oxides is negligibly small in sodium tetraborate solutions in comparison with that in acid or strong alkaline solutions. Buchanan et al. [48] studied the layer influences on the PbO_2 / PbO equilibrium in a 0.1 M $\text{Na}_2\text{B}_4\text{O}_7$ solution. Peter [49] used electrochemical and spectroscopic methods to show the reduction of thin electro-deposited films of α - PbO_2 in aqueous solutions.

Curves in Fig. 6 depict the behavior of the lead electrode in 0.1 M $\text{Na}_2\text{B}_4\text{O}_7$ [37]. The lead electrode was polarized in the potential range from -2.0 to 1.26 V (using a sweep rate of 10 mV s^{-1}).

Cyclic voltammograms of the lead electrode are very similar to voltammograms obtained by Buchanan et al. [48]. The anodic peaks correspond to the reactions leading to the formation of PbO and PbO_2 [48]. The respective cathodic peaks

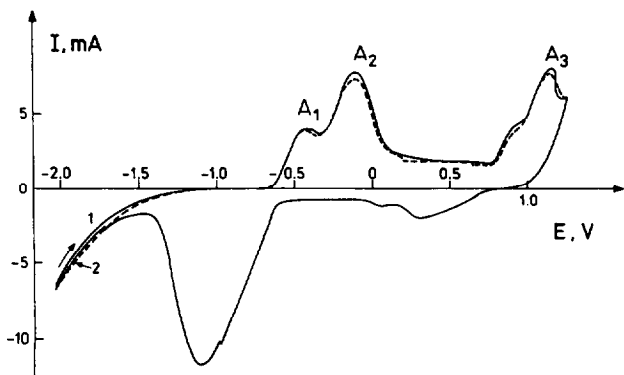


Fig. 6. Cyclic voltammograms of a metallic lead electrode in 0.1 M $\text{Na}_2\text{B}_4\text{O}_7$. Sweep rate: 10 mV s^{-1} . (—) first, and (---) next sweep.

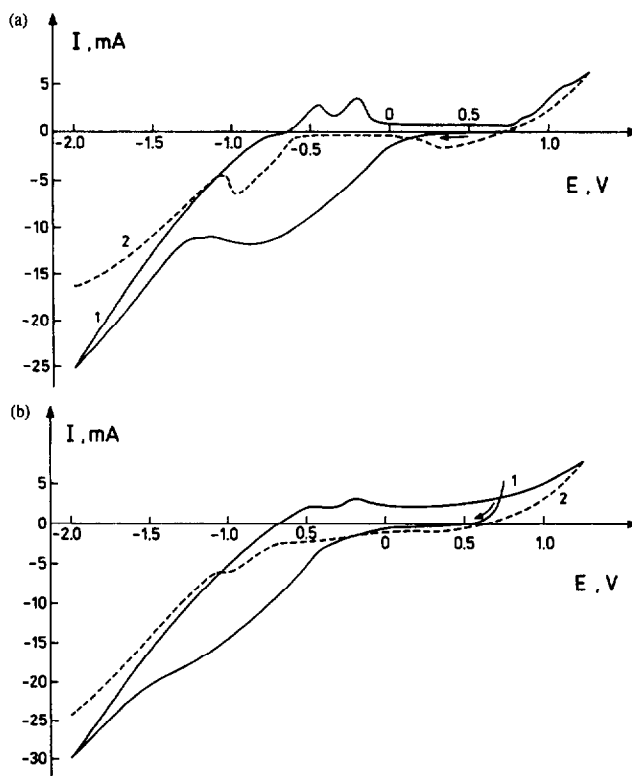


Fig. 7. Cyclic voltammograms of (a) PbO_2 /RVC, and (b) PbO_2 /Pt/RVC electrodes in 0.1 M $\text{Na}_2\text{B}_4\text{O}_7$. Sweep rate: 10 mV s^{-1} . (—) first, and (---) next sweep.

originate from currents due to the reduction of PbO_2 and PbO to metallic lead. According to Ref. [48], the peak labelled as A_1 is responsible for the formation of lead borate and peak A_2 represents the formation of PbO . The following anodic peak, denoted as A_3 , is attributed to the formation of PbO_2 .

Curves in Fig. 7(a) and (b) reflect the behavior of the PbO_2 /RVC (Fig. 7(a)) and PbO_2 /Pt/RVC (Fig. 7(b)) electrodes in 0.1 M $\text{Na}_2\text{B}_4\text{O}_7$. The electrodes were polarized in the potential range from -2.0 to 1.26 V (using a sweep rate of 10 mV s^{-1}). The peaks on the voltammograms are not well formed (especially in the cathodic sweep). This might be a result of an irreversible surface reaction between borate and lead oxides. It is possible that the electrode covered previously with lead dioxide is more sensitive to the reaction with borate than is that covered with lead during the oxidation to lead oxide. It was found before [37] that there is no fundamental difference between the electrochemical behavior of pure lead deposited on RVC or on the Pt/RVC matrix in borate solutions [37]. Differences are great between pure lead and PbO_2 deposited on RVC and Pt/RVC. This may be due to the irreversible deposition of borate on the surface of lead dioxide. Also, it seems that platinum has some influence on the surface processes of the electrodeposited lead [37] and PbO_2 .

3.3. Acidic solution

It is likely that an intermediate oxide phase leads to the formation of PbSO_4 and β - PbO_2 in H_2SO_4 while the structural

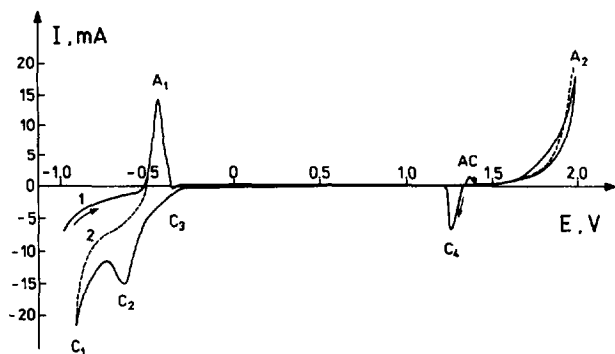


Fig. 8. Cyclic voltammograms of a pure lead electrode in 0.5 M H_2SO_4 solution. Sweep rate: 10 mV s^{-1} . (—) first, and (---) next sweep.

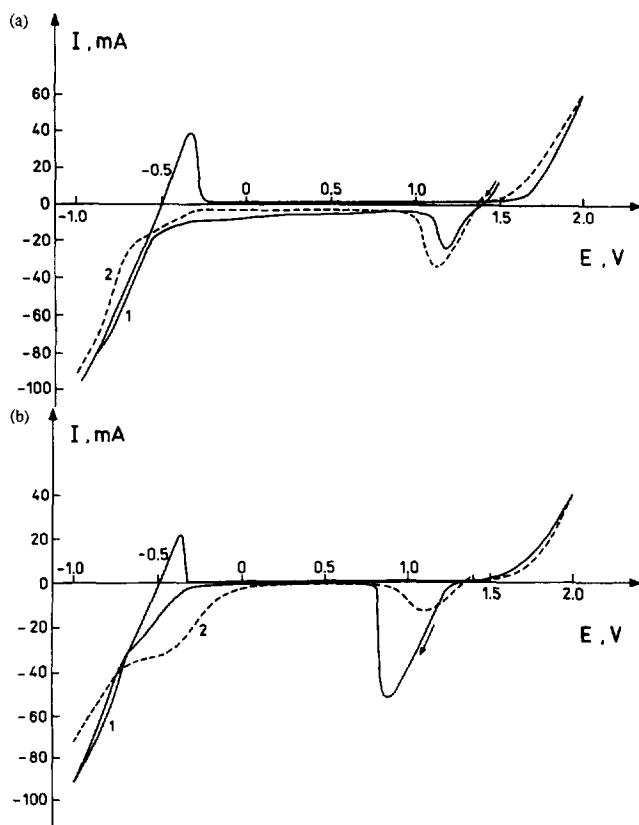


Fig. 9. Cyclic voltammograms of (a) PbO_2/RVC and (b) $\text{PbO}_2/\text{Pt}/\text{RVC}$ electrodes in 0.5 M H_2SO_4 solution. Sweep rate: 10 mV s^{-1} . (—) first, and (---) next sweep.

changes during the reduction of PbSO_4 are apparently complex. As in Ref. [37] we show also the cyclic voltammograms of the metallic lead electrode (Fig. 8) which were recorded in a 0.5 M H_2SO_4 solution in the potential range from -1.00 to 2.00 V (versus SCE) using a sweep rate of 10 mV s^{-1} .

According to the Refs. [50–59] the peaks obtained correspond to the following surface reactions [37]: A_1 is the results of lead sulfate formation; A_2 stands for the oxygen evolution that occurs together with the creation of $\beta\text{-PbO}_2$ (in the potentials region from 1.5 to 2.0 V). The small anodic peak AC is due to molar volume changes during conversion of $\beta\text{-PbO}_2$ to PbSO_4 . C_4 is the result of PbO_2 reduction to PbSO_4 . The reduction of PbO (C_3) and of PbSO_4 (C_2) pro-

ceeds to metallic lead. At the potential of about -1.0 V (C_1) the evolution of hydrogen begins to occur.

Shown in Fig. 9(a) and (b) are the cyclic voltammograms obtained for PbO_2 deposited on RVC and Pt/RVC matrices. The curve obtained for the PbO_2/RVC electrode is similar to the curve of lead given in Fig. 8. This curve is also similar to the voltammogram showed earlier for Pb/RVC [37]. On the other hand, in comparison to the cyclic voltammograms obtained in basic solutions (0.1 M NaOH and 0.1 M $\text{Na}_2\text{B}_4\text{O}_7$), the currents obtained during cycling polarization of PbO_2 deposited on RVC are several times higher than those on the metallic lead electrode. The same effect was observed for the Pb/RVC electrode [37]. As is expected the real surface areas of the resulting matrices increase following the deposition of platinum on the RVC (platinum effectively increases the real surface area). The fact that the density current, obtained during cycling polarization $\text{PbO}_2/\text{Pt}/\text{RVC}$ electrode, is smaller than that of the PbO_2/RVC electrode implies an opposite effect. Judging from the values of currents obtained during potential cycling, PbO_2/RVC (like Pb/RVC [37]) is clearly superior as a high surface electrode in comparison with $\text{PbO}_2/\text{Pt}/\text{RVC}$ (Pb/RVC [37]). The shape of the voltammogram obtained for $\text{PbO}_2/\text{Pt}/\text{RVC}$ is similar to the cyclic voltammograms for $\text{Pb}/\text{Pt}/\text{RVC}$ [37], in both cases the cathodic peak (showed in Fig. 8 as C_4) is much greater than that for electrodes obtained after deposition of PbO_2 on RVC (and lead [37]). This effect has to be due to the influence of the platinum background. As in the case of Pb/RVC behavior in sulfuric acid [37], at a potential of about -1.0 V (C_1) the evolution of hydrogen begins to occur. The cathodic currents at negative potentials (reduction of PbO and PbSO_4 to solid lead, and gaseous hydrogen evolution) tend to overlap due to iR drop of porous RVC (high current densities).

It has been noted that during one week, at ambient temperature, we have not observed any change in weight of the PbO_2/RVC electrode material which means that under these conditions the reaction between PbO_2 and RVC is rather negligible.

4. Summary

1. Reticulated vitreous carbon constitutes as a very good matrix for depositing PbO_2 (and lead [37]) onto its surface.
2. The electrochemical performance of the RVC substrate covered with PbO_2 (as lead on RVC [37]), is almost identical to the behavior of metallic lead covered with PbO_2 in basic and acidic solutions.
3. A PbO_2 electrode is more sensitive for borate solutions than lead during oxidation to PbO_2 . The product of the PbO_2 reactions with borate anions is more irreversible than surface borates generated on the lead electrode.
4. Significant effects of the matrix material–platinum on the electrochemistry of deposited PbO_2 have been observed

in all solutions studied (0.1 M NaOH, 0.1 M Na₄B₄O₇ and 0.5 M H₂SO₄).

Acknowledgements

This work was financially supported by the Committee for Scientific Research (KBN), Poland, Nr. 2P 303.005.04

The authors would like to express their thanks to Alfred Nowacki, M.Sc. from Central Laboratory Batteries and Cells (CLAiO) in Poznań for X-ray diffraction measurements and discussion of the results.

References

- [1] *Reticulated Vitreous Carbon (RVC)*, Chemometrics International, Ann Arbor, MI, USA, *Bulletin* 176, 1976.
- [2] J. Wang, *Electrochim. Acta*, 26 (1981) 1726, and Refs. therein.
- [3] A.N. Strohl and D.J. Curan, *Anal. Chem.*, 51 (1979) 353.
- [4] A.N. Strohl and D.J. Curan, *Anal. Chem.*, 51 (1979) 1054.
- [5] A.N. Strohl and D.J. Curan, *Anal. Chem.*, 51 (1979) 1050.
- [6] W.J. Blaedel and Z. Yim, *Anal. Chem.*, 52 (1980) 564.
- [7] W.J. Blaedel and J. Wang, *Anal. Chem.*, 51 (1979) 799.
- [8] V.E. Norvell and G. Mamantov, *Anal. Chem.*, 49 (1977) 1470.
- [9] T.P. De Angelis and W.R. Heineman, *J. Chem. Educ.*, 53 (1976) 594.
- [10] A.N. Strohl, *Diss. Absir. Int. B*, 40 (1979) 1149.
- [11] H.E. Ward and C. Hussey, *Anal. Chem.*, 59 (1987) 213.
- [12] S. Zamponi, M. DiMarino, R. Marassi and A. Czerwiński, *J. Electroanal. Chem.*, 248 (1988) 341.
- [13] S. Zamponi, A. Czerwiński and R. Marassi, *J. Electroanal. Chem.*, 266 (1989) 37.
- [14] S. Zamponi, A. Czerwiński, G. Gambini and R. Marassi, *J. Electroanal. Chem.*, 332 (1992) 63.
- [15] J. Wang, *Stripping Analysis; Principles, Instrumentation and Applications*, VCH, Deerfield Beach, FL, 1985, and Refs. therein.
- [16] G. Dryhurst and D. McAllister, in PT. Kissinger and W.R. Heinemann (eds.), *Laboratory Techniques in Electroanalytical Chemistry*, Marcel Dekker, New York, 1984, pp. 289–319.
- [17] A. Czerwiński, R. Marassi and J. Sobkowski, *Ann. Chim. (Roma)*, 74 (1984) 861.
- [18] A. Czerwiński, J. Sobkowski and R. Marassi, *Anal. Lett.*, 18 (1985) 717.
- [19] A. Czerwiński, *Anal. Lett.*, 20 (1987) 503.
- [20] A. Czerwiński, R. Marassi and S. Zamponi, *J. Electroanal. Chem.*, 316 (1991) 211.
- [21] A. Czerwiński, *Pol. J. Chem.*, 69 (1995) 699.
- [22] M. Berrettoni, S. Zamponi, R. Marassi and A. Czerwiński, *Ann. Chim. (Roma)*, 76 (1986) 171.
- [23] D. Calasanzio, C. Sorana, S. Zamponi and R. Marassi, *Ann. Chim. (Roma)*, 73 (1983) 161.
- [24] S. Zamponi, M. Berrettoni and R. Marassi, *J. Electroanal. Chem.*, 219 (1989) 153.
- [25] J. Osteryoung and J.J. O'Dea, in A.J. Bard (ed.) *Electroanalytical Chemistry*, Vol. 14, Marcel Dekker, New York, 1986, pp. 209–303.
- [26] S.P. Kounaves, J.J. O'Dea, P. Chandrasekhar and J. Osteryoung, *Anal. Chem.*, 59 (1987) 386.
- [27] S.P. Kounaves, J.J. O'Dea, P. Chandrasekhar and J. Osteryoung, *Anal. Chem.*, 58 (1986) 3199.
- [28] M. Matlose and J. Newman, *J. Electrochem. Soc.*, 133 (1986) 1850.
- [29] W.J. Blaedel and J. Wang, *Anal. Chem.*, 51 (1980) 76.
- [30] G.W. Schieffer, *Anal. Chem.*, 52 (1980) 1994.
- [31] J. Wang and H.D. Dewald, *J. Electrochem. Soc.*, 130 (1983) 1814.
- [32] J. Wang, H.D. Dewald, *Anal. Chem.*, 55 (1983) 933.
- [33] J.H. Christie and R.A. Osteryoung, *Anal. Chem.*, 48 (1976) 869.
- [34] C. Ponce de Leon and D. Pletcher, *Electrochim. Acta*, 41 (1996) 533.
- [35] E. Beinrohr, M. Nemeth, P. Tshopel, G. Tolg, *Fresenius' Z. Anal. Chem.*, 344 (1992) 93.
- [36] P. Tissot and M. Fragniere, *J. Appl. Electrochem.*, 24 (1994) 509.
- [37] A. Czerwiński and M. Żelazowska, *J. Electroanal. Chem.*, in press.
- [38] A. Czerwiński, J.R. Schrader, H.B. Mark, Jr., *Analyt. Chem.*, 56 (1984) 1039.
- [39] D. Pavlov, S. Zanova and G. Papazov, *J. Electrochem. Soc.*, 124 (1977) 1522.
- [40] J. Minczewski and Z. Marczenko, *Chemia Analityczna*, PWN, Warsaw, 1965.
- [41] *Poradnik Galwanotechnika*, PWN, Warsaw, 1985.
- [42] Ch. Cominellis and E. Platiner, *J. Appl. Chem.*, 12 (1982) 399.
- [43] S. Tabat, A. Nowacki and B. Szcześniak, *J. Power Sources*, 31 (1990) 339.
- [44] B. Centeno, M. Tascón, M.D. Vazquez and P. Sanchez Batanero, *Electrochim. Acta*, 36 (1991) 277.
- [45] V.I. Birss and T. Shevalier, *J. Electrochem. Soc.*, 137 (1990) 2643.
- [46] P. Veluchamy, M. Sharon, H. Minoura, Y. Ichihashi and K. Basavaswaran, *J. Electroanal. Chem.*, 344 (1993) 73.
- [47] K.R. Bullock, *J. Power Sources*, 51 (1994) 1.
- [48] J.S. Buchanan, N.P. Freestone and L.M. Peter, *J. Electroanal. Chem.*, 182 (1985) 383.
- [49] L.M. Peter, *J. Electroanal. Chem.*, 144 (1983) 315.
- [50] J.G. Sunderland, *J. Electroanal. Chem.*, 71 (1979) 341.
- [51] S. Fletcher and D.B. Matthews, *J. Electroanal. Chem.*, 126 (1981) 131.
- [52] H.S. Panesar, in D.H. Collins (ed.), *Power Sources 3*, Oriel Press, Newcastle upon Tyne, 1971.
- [53] Y. Yamamoto, K. Fumino, T. Ueda and M. Nambu, *Electrochim. Acta*, 37 (1992) 199.
- [54] Y. Yamamoto, M. Matsuoka, M. Kimoto, M. Uemura and C. Iwakura, *Electrochim. Acta*, 41 (1996) 439.
- [55] P. Ruetschi, *J. Electrochem. Soc.*, 120 (1973) 331.
- [56] D. Pavlov and N. Iordanov, *J. Electrochem. Soc.*, 117 (1970) 1103.
- [57] D. Pavlov and R. Papova, *Electrochim. Acta*, 15 (1970) 1483.
- [58] M. Fleischmann and H.R. Thirsk, *Trans. Faraday Soc.*, 51 (1955) 71.
- [59] R.L. Deutscher, S. Fletcher and J.A. Hamilton, *Electrochim. Acta*, 31 (1986) 585.