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Dedicated to prof. dr. I. C. Popescu
on the occasion of his 70th anniversary

SPECTRAL GRAPHITE AS ELECTRODE MATERIAL FOR THE ALL-VANADIUM REDOX FLOW BATERY

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ABSTRACT. The ability of unmodified or PbO_2 coated spectral graphite (SG), to act as positive electrode in an all vanadium redox flow battery was tested. Our results showed that the unmodified SG requires simple pretreatment and is efficient in terms of current due to a large active area, 4 time greater that the geometrical one. The PbO_2 deposits were grown on surfaces that previously received only basic treatment, but present a poor stability. In all experiments, large separations of anodic and cathodic peak potentials (between 118 and 1015 mV) were observed, proving the irreversibility of the V^{V} to V^{IV} redox couple on all studied materials.

Keywords: *all vanadium battery, spectral graphite, cyclic voltammetry*

INTRODUCTION

Electrochemical power sources are an important alternative tool for energy converting and storage. A special category is the Redox Flow Batteries (RFB) - secondary batteries that employ solvated redox couples. The marked interest for RFB displayed during recent years owes to the ever increasing necessity for storing the energy, especially that generated by the renewable, fluctuating sources as solar or wind power [1-4].

All vanadium redox flow battery (VRFB) is particularly attractive, because it avoids any irreversible cross-contamination, since the active redox couples in the two sides of the cell employ the same chemical element. The $V^{II/III}$ couple operates in the negative half-cell (eq. 1) and $V^{IV/V}$ in the positive half-cell (eq. 2).

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$$V^{III} + e^{-} \leftrightarrow V^{II} \qquad E^{0} = -0.26\,V/EHN \qquad (1)$$

$$(V^{IV}O)^{2+} + H_2O \leftrightarrow (V^{V}O_2)^{+} + 2H^{+} + e^{-} \qquad E^{0} = +1.00\,V/EHN \qquad (2)$$

However, achieving high performances for VRFB strongly depends on the electrode material, which should ensure, simultaneously, as low as possible overpotentials for the reactions (1) and (2) and as high as possible overpotentials for the water decomposition reactions (3) and (4) that inherently occur in aqueous solutions:

$$H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^{+} + 2e^{-} \qquad E^{0} = +1.23\,V/EHN \qquad (3)$$

$$H_2O + e^{-} \rightarrow \tfrac{1}{2}H_2 + HO^{-} \qquad E^{0} = -0.83\,V/EHN \qquad (4)$$

Of outmost importance for the performance of all vanadium redox flow battery is the electrode material. A vast range of electrode materials was evaluated as both positive and negative electrodes for the VRFB. Many of the materials tested were carbon-based and graphite, in particular [5,6]. The properties that make graphite desirable are: good electronic conduction, good stability in highly acidic solutions and under a large window of potentials, marked porosity that ensures quite large reactive surface area by providing a multitude of redox reaction sites [7], low cost and easy manufacturing.

In general, the carbonaceous materials were found to perform well in the negative half of the cell [5,8]. Some deterioration was observed when they were used in the positive half-cell, attributed to the slow oxidation of the surface as a result of oxygen evolution during cell overcharge [9].

Some other electrode materials that were tried out include lead, gold, platinum, platinized titanium or other consecrated dimensionally stable anodes (DSAs), and gave mixed results [8]. Lead based electrodes received some special attention, being less costly and relatively stable in sulfuric acid systems. However, Pb becomes passivated in the potential range where the $V^{IV/V}$ redox couple reactions occur [5].

Nowadays, graphite is the typical choice for the VRFB electrodes. In addition to its above mentioned advantages, it provides satisfactorily large overpotentials towards the parasitic reactions (3) and (4). Of the various types tried out, such as rods, plates, cloths and felts, the latter are often preferred, based on their large specific surface. In order to achieve longer lifetime and superior energetic capacity (higher currents), there is a continuous focus on the improvement of the electrode material.

Several ways have been explored to this end, such as the use of additives [10], thermal treatment [5], or oxidative treatment [11] of the graphite surface. The electrode surface modification has been also tried out, in order to enhance the electrochemical activity of the vanadium redox couples. Usually, it was done by electrodeposition of noble metals such as Pt, Au, Pd, or Ir [12-14] but Pb was also considered for the task.

Some recent work reports a doubling of the peak current density for the $V^{IV/V}$ system on a graphite felt electrode modified by coating with a layer of PbO_2 of approximately 2 μm, through pulse electrodeposition [15], but this improvement was only briefly explored. During our attempts to obtain cheap and improved electrodes for the positive half-cell, we decided to investigate the effect of spectral graphite (SG) modification with PbO_2. Over the graphite felt, SG presents better mechanical properties and enhanced purity; therefore, we considered it a promising choice as base material for PbO_2 deposition. In line with the low costs target, we also aimed to keep the pretreatment of the electrode surface at a minimal level. This paper reports on our results concerning the electrochemical behaviour of unmodified and modified SG electrodes towards the V^{IV}/V^{V} redox couple.

RESULTS AND DISCUSSION

As pointed out, the intended goal was to obtained and study PbO_2 modified electrodes, by using the spectral graphite (SG) as support. However, tests on the unmodified SG were required first.

Our studies were undertaken at 25 ºC in an aqueous solution containing 0.2 M total vanadium (0.1 M V^{IV} and 0.1 M V^{V}) in 2 M H_2SO_4, by using the cyclic voltammetry (CV). The voltammograms were recorded at 6 scan rates (v), between 5 and 100 mV/s, (always starting with the highest rate), over the 0.5 V to 1.5 V potential range (measured *vs.* an $Ag/AgCl/KCl_{sat}$ reference electrode). We did not to use lower potentials in order to avoid the reduction of V^{IV} to V^{III}.

Electrochemical behaviour of unmodified and pretreated SG electrodes

The first SG electrode (prepared as described in the experimental section) was used for measurements immediately after insertion in the solution, and exhibited an irreproducible behaviour.

Such outcome was hardly unexpected, since it is documented that the surface of graphite suffers changes in strongly acidic media [5] during the first potential scans. The changes consist on the formation of oxygen moieties which act as mediators for the electron transfer, by facilitating the adsorption of vanadium ions [11]. This process is regarded as an activation of the surface.

Repeated tests were made in order to establish the conditions in which the activation is completed (an equilibrium is reached at the surface), expressed as reproducible response of the electrode. This was accomplished if the freshly prepared electrode was first allowed to complete about 25 cycles over the 0.0 to 1.5 V range of potential at a scan rate of 50 mV/s, the first 15 of them performed in a solution of 2 M H_2SO_4 and the remaining 10 ones in the solution containing the vanadium species.

Figure 1 shows the cyclic voltammograms obtained on an SG electrode (SG I) pretreated as described above. At any scan rate, the second and third cycles overlapped very well, proving once more that the electrode surface has reached a stabilized state.

A second electrode (SG II), which was pretreated 15 cycles in H_2SO_4 followed by 20 cycles in the acidic V^{IV} - V^{V} solution, was tested with very similar results.

The pretreatment in the vanadium free H_2SO_4 solution proved to be essential, because other electrodes, treated for 35 cycles or more only in the vanadium containing solution, did not reach reproducible responses.

As illustrated in Figure 1, unusual high currents were registered for both the oxidation and the reduction peaks (1.8 to 8.1 mA for the anodic scan and 1.0 to 6.0 mA for the cathodic scan). Similar currents recorded on a graphite electrode are reported in literature when a 15 times more concentrated solution was used [10].

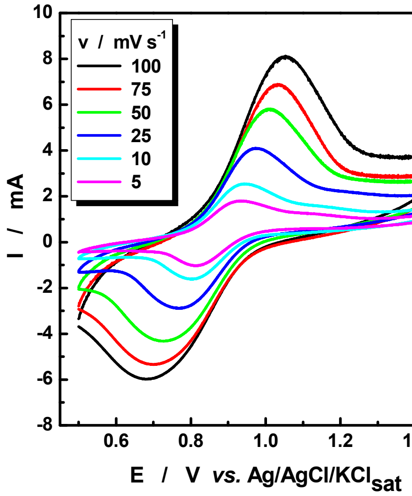

Figure 1. CV curves recorded in 0.1 M V^{IV} and 0.1 M V^{V} in aqueous 2 M H_2SO_4 on a spectral graphite electrode (SG I) at various scan rates, at T = 298 K

The cyclic voltammograms (Figure 1) also show some asymmetry and marked separation of the peaks. As known, for a totally irreversible process, the peak potential (E_p) is a function of the scan rate (v), shifting in a negative direction (for reduction) by an amount 1.15RT/nF (or 30/n mV at 25°C) for each tenfold increase in v [16]. Owing to the peak separation observed (ranging between 118 mV at v = 5 mV/s to 369 mV at v = 100 mV/s) the $V^{IV/V}$ redox process can be best characterized as irreversible.

Slightly higher peak separation (164 to 448 mV) and also marginally higher reduction peak currents (1.3 to 6.1 mA) were obtained with SG II. The oxidation peak currents stayed virtually the same (1.8 to 7.9 mA).

As shown in Figure 2, the dependences of the peak current on the square root of the scan rate for both electrodes proved to be linear, leading to the conclusion that the electrode process is diffusion controlled.

For an irreversible process, the equation describing the peak current takes the form [16]:

$$i_p = 0.4958\left(\frac{n^3F^3}{RT}\right)^{1/2}\alpha^{1/2}AC_0D^{1/2}v^{1/2} \tag{5}$$

where: i_p = peak current [A]; n = number of electrons transferred; F = Faraday constant [A s mol^{-1}]; R = Gas constant [J K^{-1} mol^{-1}]; T = temperature [K]; α = transfer coefficient (dimensionless); A = electrode area [cm^2]; C = concentration [mol cm^{-3}]; D = diffusion coefficient [cm^2 s^{-1}] and v = scan rate [V s^{-1}].

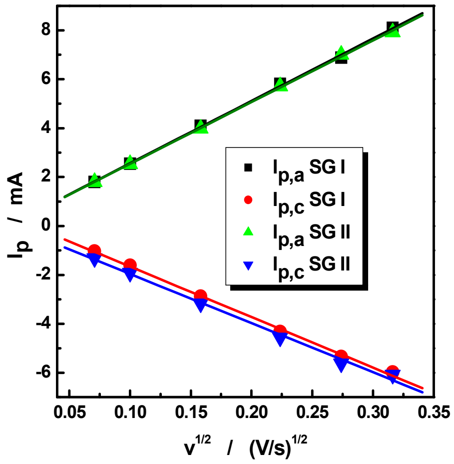

Figure 2. The oxidation (■▲) and reduction (●▼) peak current as a function of the square root of scan rate, for the two SG pretreated electrodes

The slopes of the plots in Figure 2 are dependent on the diffusion coefficient (D) and can be used to compute it. However, applying this treatment (with α = 0.5), D values of $7.28 \cdot 10^{-5}$ or $7.16 \cdot 10^{-5}$ cm^2 s^{-1} from the oxidation peaks and of $4.52 \cdot 10^{-5}$ or $4.78 \cdot 10^{-5}$ cm^2 s^{-1} from the reduction peaks were obtained with SG I and SG II, respectively. These values are in obvious disagreement with those reported in the literature [6,17], which are 20-50 times lower. However, these results were not surprising, considering the high current values recorded.

To shed more light on the matter, a platinum electrode disc with a surface of 0.0314 cm^2 was tested in our vanadium solution. The potential scan range was extended, from -0.1 V to 1.6 V, in order to allow a complete development of the peaks. For the platinum electrode, no activation was required. The second and third cycles of the voltammograms completely overlapped at all of the tested scan rates (between 25 and 200 mV/s). The CV curves obtained with this setup are presented in Figure 3. The irreversibility of the reaction is much more evident here (ΔE of 868 to 1015 mV), hence equation (5) was employed again to compute the diffusion coefficient D.

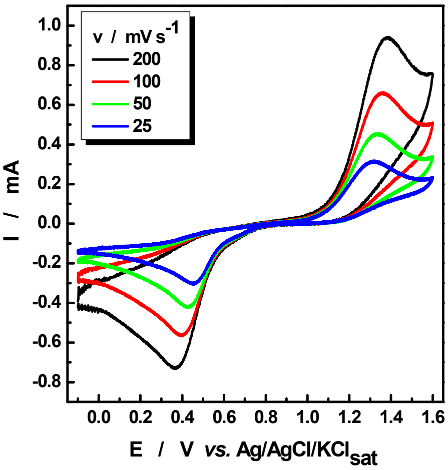

Figure 3. CV curves on a platinum disc (conditions like in Figure 1)

The values obtained were $2.68 \cdot 10^{-6}$ cm^2 s^{-1} from the anodic peaks and $1.22 \cdot 10^{-6}$ cm^2 s^{-1} from the cathodic ones. These values compare fairly well with those listed in literature, for instance $1.4 \cdot 10^{-6}$ cm^2 s^{-1} on glassy carbon, $2.4 \cdot 10^{-6}$ cm^2 s^{-1} on carbon paper and pyrolytic graphite, or $3.9 \cdot 10^{-6}$ cm^2 s^{-1} on plastic formed carbon [6, 17].

The difference between the two computed values may be a result of some interference of the water oxidation (eq. 3) in the anodic region. It is also conceivable that the difference in the volume of the two oxygenated vanadium oxoanions, and of the species that they form with H_2SO_4 in aqueous medium may result in slightly different diffusional properties.

The explanation for the high currents obtained on the SG electrodes must lay, therefore, in the value of the active surface, which should be higher. Indeed, some advancement of the solution in the pores of the material cannot be ruled out.

An estimation of the effective area of our electrode can be made assuming that the diffusion coefficients on the SG electrodes can be substituted by those obtained on platinum. Than, the ratio of the slopes obtained from the plots shown in Figure 2 is proportional to the ratio of the two active surfaces (eq. 6):

$$\frac{\text{slope}_{SG}}{\text{slope}_{Pt}} = \frac{A_{SG}}{A_{Pt}} \tag{6}$$

Keeping for each side of the reaction (oxidation and reduction) the diffusion coefficient as found, estimate values for the effective surface of SG were computed. The results obtained were 0.261 and 0.312 cm^2 with SG I and 0.259 and 0.303 cm^2 with SG II, averaging to 0.28 ± 0.03 cm^2. This is about 4 times higher than the geometrical surface (0.0707 cm^2).

Electrochemical behaviour of PbO_2 modified SG electrodes

Based on the Faraday law, we evaluated that a current of 1 mA applied for 60 s was required to deposit a layer of approximately 1 μm PbO_2 on the geometrical surface of our electrode. Two electrodes were prepared and tested, one coated with 1 μm (SG/Pb I) and the other with 2 μm of PbO_2 (SG/Pb II)

Prior to use, each PbO_2 coated electrode was pretreated for a number of 10 or 16 cycles respectively, over the 0.0 V to 1.5 V potential range, at 50 mV/s in the vanadium containing acidic solution. As the depositing of PbO_2 was carried out in acidic medium, and the surface was already coated, the H_2SO_4 pretreatment was not considered necessary. The CV tests were completed under the same conditions as those for the non coated electrodes.

The set of measurements made on SG/Pb I seemed to fall satisfactorily on the expected pattern. The CV curves obtained with SG/Pb I (Figure 4) show worse symmetry and slightly higher separation of the peaks (ΔE between 188 and 567 mV) as compared to those of SG I (Figure 1) or SG II, arguing even stronger for the irreversibility of the redox process.

The measured currents for the anodic and cathodic peaks were still high, (1.63 to 6.09 and 1.66 to 7.25 respectively) but not higher than those obtained with the non coated electrodes. Further processing of the data led to results similar to those for the unmodified SG electrodes. An effective area of the electrode of 0.26 ± 0.02 cm^2 resulted (0.235 and 0.277 cm^2 from oxidation and reduction peaks respectively).

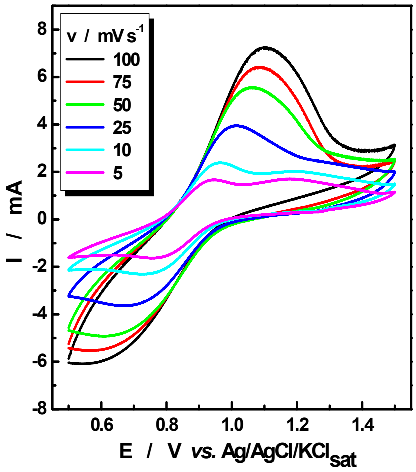

Figure 4. CV curves for a PbO_2 coated SG electrode (SG/Pb I) (conditions like in Figure 1)

The electrode SG/Pb II exhibited irregular behaviour and, upon check, did not stand the test of reproducibility. This led us to suspect that the straightforward deposition without any pretreatment of the graphite surface does not result in a lasting coating and the PbO_2 layer is removed from the surface. Moreover, $PbSO_4$ may be formed, leading to partial blockage of the active centers of the surface.

Some microscopic images (Figure 5) seem to give further support to the instability hypotheses.

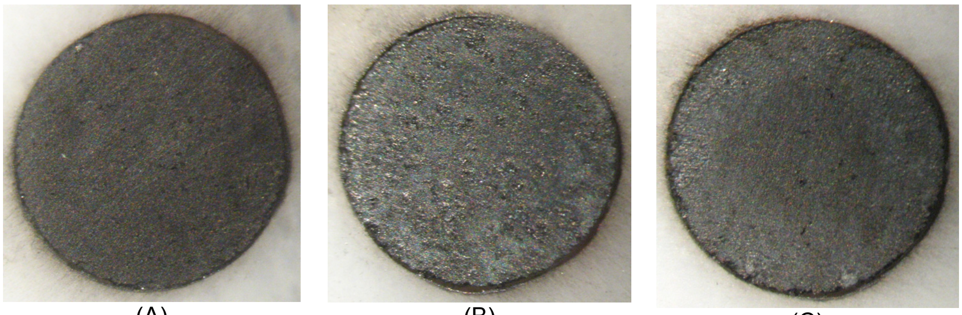
(A) (B) (C)

Figure 5. Microscopic images of SG/Pb II: the unmodified SG surface (A), after depositing a *approx.* 2 μm PbO_2 layer on the surface (B) and after the completion of the measurements in the 0.2 M vanadium in 2 M H_2SO_4 solution (C).

It appears that, after the completion of the set of measurements, either the graphite surface of the SG/Pb II is visible again or some different deposits were formed on top of the PbO_2 layer (Figure 5.C).

In light of this, it is probable that the thinner PbO_2 coating of SG/Pb I had been quickly removed during the 10 cycles in the V^{IV} – V^{V} solution completed prior to measurements and the activation of the graphite surface was almost achieved. This explains the quite similar results to those obtained on non coated SG electrodes.

CONCLUSIONS

The spectral graphite is a promising electrode material, in terms of achieving high currents in VRFB in a simple way. Just like with felts, its active surface is higher than the geometrical one, owing to its porosity. Indeed, an effective surface 4 times higher than the geometrical one was found in our studies. Since reproducible behaviour could be obtained and with relatively little pretreatment, further efforts to study the properties of SG electrodes seem justified. Moreover, better mechanical properties may be envisioned, but studies of stability in time and further optimization of the activation procedure are required.

The attempts to modify the SG surface by electrodeposition of PbO_2 did not result in any improvement of the current. However, the PbO_2 layer was deposited on a surface that did not receive specific pretreatment and, under the circumstances, proved unstable. More efforts should be made in the direction of pretreatment of the surface prior to PbO_2 coating.

For the tested electrodes, large separations of anodic and cathodic peak potentials were observed, ranging between 118 and 567 mV for SG, 188 and 567 mV for SG/Pb, or 868 and 1015 mV for Pt, proving the irreversibility of the V^{V} to V^{IV} redox couple on all materials.

EXPERIMENTAL SECTION

The reagents used (solid $C_2H_2O_4$, $Pb(NO_3)_2$, NaF and 98 % H_2SO_4 and 0.1 M HNO_3 solutions) were all of analytical purity, and used as received (Merck, Aldrich).

A 0.2 M solution of VO_2^+ was prepared by dissolving the appropriate amount of V_2O_5, under constant stirring and heating, in a 2 M H_2SO_4 aqueous solution. A solution of 0.2 M VO^{2+} was prepared in a similar manner, with the difference that a stoichiometric amount of oxalic acid was added, to achieve the reduction of V^V to V^{IV}. Equal volumes of the two solutions were mixed to obtain the final 0.1 M VO_2^+ and 0.1 M VO^{2+} in 2 M H_2SO_4 solution, which was employed in the experiments.

The electrochemical measurements were performed using a computer-controlled multipotentiostat, model DXC 238, (Datronix Computers, Romania). The application used for experiment control and data acquisition has been developed in our laboratory using the LabView 8.5 (National Instruments, USA) software. The stored data have been further processed using the Origin8 software (OriginLab, USA).

A three-electrode electrochemical glass cell (50 mL) was used for the cyclic voltammetry measurements. The working electrodes (WE) were made from spectral graphite (Ringsdorff-Werke GmbH, Germany) rods (∅ = 3 mm, L = 25 mm) fixed in a Teflon holder, specially designed to allow for easy replacement of the electrode before each experiment. The surface of the each new graphite WE was first polished on a 1200 grit abrasive paper and abundantly washed with distilled water. The platinum disc electrode (∅ = 2 mm) was also mirror polished with alumina paste (0.5 µm).

Spectral graphite rod (∅ = 3 mm, L = 80 mm) was used as counterelectrode (CE), while an Ag/AgCl/KCl_{sat} system was used as the reference electrode (RE) (E_{RE}=0.197 V *vs.* ENH).

The PbO_2 coatings were obtained by galvanostatic electrodeposition, from an aqueous solution containing 0.23 M $Pb(NO_3)_2$, 0.03 M HNO_3 and 0.03 M NaF [15]. The cell used consisted of the electrode to be coated, a graphite plate with a high surface (6 cm^2) as CE and the Ag/AgCl/KCl_{sat} system as RE, all dipped in the $Pb(NO_3)_2$ solution. Besides the polishing and washing, the electrode surface was dried under argon current prior to the PbO_2 electrodeposition.

Before each measurement at a new scan rate, the solution was stirred for 10 seconds (with a magnetic stirrer), in order to ensure the removal from the surface of the WE of any oxygen bubbles or redox products formed during previous scans.

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