

A METHOD FOR INVESTIGATION OF THE STATIONARY ELECTROCHEMICAL KINETICS OF O₂ RECOMBINATION IN VALVE REGULATED LEAD ACID (VRLA) BATTERIES

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Abstract

At the end of charge water is decomposed and oxygen is evolved on the positive plates of lead-acid cells. Since in VRLA batteries the pores of the AGM separator are only partially filled with electrolyte, the evolved oxygen gas may diffuse towards the surface of the negative plate where it reacts to forming water. This oxygen recombination reaction is the major step in the closed oxygen cycle (COC). The operation of the COC inside the lead acid cells substantially reduces the water losses and is a key point for VRLA batteries operation. The aim of this study is to investigate the dependence of the O₂ recombination current on the negative plate potential at steady state conditions and to determine the efficiency of the COC at this potential. The electrochemical data obtained for the efficiency of the COC showed that at temperatures up to 30°C oxygen recombination proceeds according to an electrochemical mechanism: $O_2 + 4H^+ + 4e^- = 2H_2O$.

It features two limiting stages – impeded diffusion of O₂ gas through the wetting film of electrolyte covering the surface of the negative active mass and impeded charge transfer (typical for the oxygen electrode system).

At elevated temperatures and higher polarization oxygen recombination proceeds according to a second concurrent mechanism comprising the chemical reaction among adsorbed hydrogen atoms and oxygen molecules coming from the solution.

1. Introduction

A basic requirement for portable and emergency energy sources (POEMES) is the lack of maintenance during their whole service life. In lead-acid batteries maintenance comprises periodic top-levelling for compensation of the water losses that occur due to overcharge and self discharge of the cells. Water losses are completely eliminated (under specified conditions) in valve regulated lead acid batteries (VRLAB) utilising oxygen recombination. In AGM – VRLA batteries the conventional micro porous separator (PVC, PE, hard rubber etc.) is replaced by an absorptive glass mat (AGM) made of boron-silica glass micro fibres. The electrolyte is absorbed in the pores of the separator and in the positive and negative battery plates. If the pores of the AGM separator are only partially filled with electrolyte, the evolved on the positive plates oxygen at the end of charge diffuses through the gas filled separator pores towards the surface of the negative plates, where it recombines to water according to an electrochemical mechanism:



or a chemical one:



If the rate of oxygen evolution exceeds a certain limit, the pressure in the cell increases and the normally closed valve opens and some gas is released.

The entire system of reactions including oxygen evolution, transport and recombination is called closed oxygen cycle (COC). The deeper understanding of O₂ recombination is of vital importance for the design and production of reliable VRLAB.

Depending on the object where O₂ recombination proceeds, two groups of studies can be distinguished:

- a) O₂ recombination is studied by a RDE technique at stationary conditions on smooth Pb and lead alloys electrodes [1-4];
- b) the process is investigated on the negative plates of real batteries in two ways:
 - **by measurement of the gas diffusion rate:** in these experiments the negative plates are partially dipped into electrolyte and partially exposed to an O₂ atmosphere, operating in this way as gas diffusion electrodes in potentiostatic mode. The highest oxygen diffusion rate is observed in the upper part of the meniscus formed, where the electrolyte layer has the smallest thickness and the highest conductivity [5-7];
 - **by measurement of the gas pressure:** in these studies a single negative plate (wet by electrolyte and not polarized) is put in a hermetically closed container filled with O₂. The rate indicating parameter for O₂ recombination here is the pressure derivative by time [8-10]. If a pressure gauge is mounted on the VRLA cell container and the chemical composition of the gas atmosphere in the cell is monitored in parallel, the manometric method turns into an *in-situ* method for studying the processes involved into the COC [11, 12].

In our previous paper [13] a new idea for *in-situ* studying of O₂ recombination at non stationary conditions was proposed, based on the gas flow measurements leaving a completely charged VRLA cell during constant current polarization. The goal of our work is the further development of this method by investigating the stationary dependence of the O₂ recombination rate as well as of the COC efficiency on the negative plate potential.

2. Experimental

Model VRLA cells were assembled comprising two positive and one negative (1.5 Ah) plates, separated by an AGM separator (H&V, 440 g.m⁻², BCI thickness 2.6 mm), and a Hg/Hg₂SO₄ reference electrode. The plates had dimensions of 1.7 x 60 x 51 mm and Pb-1%Sn-0.1%Ca grids. All plates were tank-formed and dry charged. 15% compression was applied to the AGM separators. The negative plate was assumed to be the working electrode and the positive plates were used simultaneously as counter-electrodes and an oxygen source.

The test cell was flooded with sulphuric acid solution with s.g. 1.27 and left to soak for 30 min. followed by the excess electrolyte removal. The cell was connected to a potentiostat/galvanostat MSTAT 4+ (ARBIN Instruments) and to a gas flow meter constructed in the Lead acid batteries department of IEES. The scheme of the gassing rate monitoring sensor is shown in Fig. 1. The outgoing gas is lead through the sensor as gas bubbles in a tube filled with water. The number of gas bubbles passed is determined by a light source / photo detector couple. When a bubble is evolved it interrupts the light beam towards the photo detector.

Each pulse is detected and recorded by the PC. The system is calibrated by counting the number of bubbles corresponding to a gas volume of 100 cm³ at an average rate of 2-3 bubbles per second. After the initial recharge, the cell was set to 10 charge-discharge cycles under the following conditions: discharge at 300 mA until the potential of the negative plate reached $\varphi^- = -0.7$ V followed by charge at 300 mA up to charge factor of $\eta_{ch} = 105\%$ and then further charge at 150 mA to $\eta_{ch} = 125\%$. In order to initiate an oxygen cycle with sufficiently high efficiency the

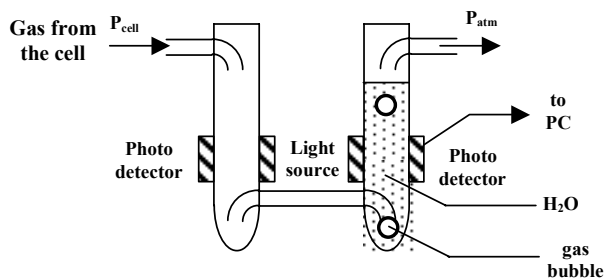


Fig. 1. Scheme of the gas flow meter.

cell was subjected to continuous overcharge until the saturation of the active block with electrolyte reached 83%. Then the kinetics of the oxygen recombination reaction was investigated through cyclic linear voltammetry (CLV) from -1.05 V to -1.30 V at a potential scan rate $0.02\text{ mV}\cdot\text{s}^{-1}$. In parallel to cyclic voltammetry the rate of the gas flow leaving the cell was measured. Since the cell was overcharged for a very long period of time, the gas composition was considered to be a stoichiometric mixture of O_2 and H_2 in a volume and mol ratio 1:2. In this case the partial current due to water loss can be calculated from the gas flow rate. The experiments were performed at two temperatures: 15 and 50°C ($\pm 0.1^\circ\text{C}$).

After recording the voltammograms at both temperatures, water was added to the cell for achieving electrolyte saturation higher than 100%. The kinetics of the processes at the negative plate at this degree of saturation was investigated under the same CLV conditions, but at potential scan rate of $0.06\text{ mV}\cdot\text{s}^{-1}$. Under these conditions the efficiency of the COC tends to zero, which allowed us to assess the contribution of the hydrogen evolution reaction to the overall current. A similar approach was used also by the authors of references [1-4] in studying the kinetics of oxygen reduction on a rotating Pb-disk electrode, where the measurements were conducted once in an oxygen-saturated electrolyte and then in an electrolyte from which oxygen has been removed prior to test.

3. Results and discussion

3.1. Dependence of the negative plate overcharge rate in a VRLAB at 15°C on the potential.

Figure 2a shows the relationships between the current and the negative plate potential at 100 and 83% saturation of the active block with electrolyte in the case of a 100% charged model cell. At 100% electrolyte saturation the current follows the Tafel equation and is considerably lower than the current at 83% saturation. This is due to the fact that, at higher electrolyte saturations, the transport of the oxygen to the surface of the negative plate is impeded because of the lack of open gas channels in the AGM separator. Thus, the main process at 100% electrolyte saturation that takes place at the negative plate during overcharge is hydrogen evolution. The high current value measured at 83% saturation is due to the concurrent processes of oxygen recombination and hydrogen evolution.

The difference in the current values measured at 83 ($I_{83\%}$) and at 100 % electrolyte saturation ($I_{100\%}$) at the same negative plate potential is the current of the electrochemical oxygen recombination process, I_{ECR} . The result of this calculation is presented in Fig. 2b. The process of oxygen recombination is impeded by the diffusion of oxygen molecules through the thin liquid film of the electrolyte that covers the surface of the negative active mass crystals and by the subsequent charge transfer during the electrochemical reaction. The correlation between current and potential of a diffusion and kinetically limited process can be expressed by the following equation:

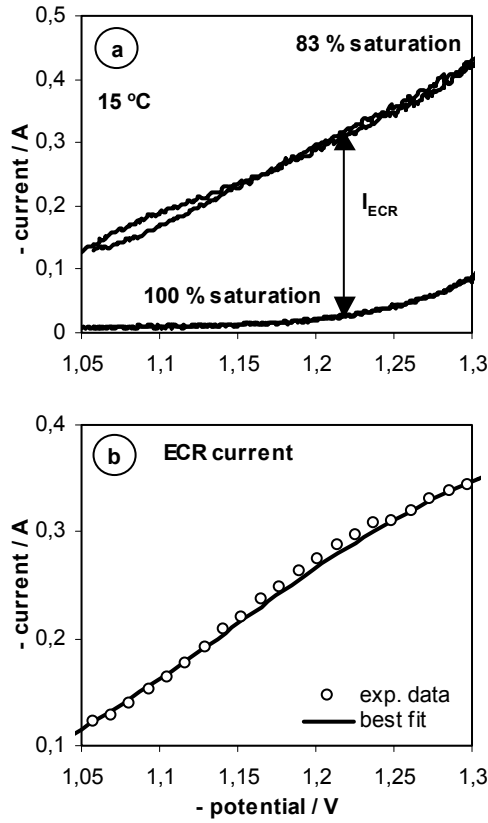


Fig. 2. (a) Current versus potential of the negative plate at 100% and at 83% electrolyte saturation of the active block at 15°C. (b) Current of electrochemical recombination of oxygen I_{ECR} versus the potential and best fit with equation (3).

$$\varphi_- = \frac{RT}{\alpha n F} \ln\left(\frac{I_0}{I_d}\right) + \frac{RT}{\alpha n F} \ln\left(\frac{I_d}{I} - 1\right) \quad (3)$$

where φ_- is the potential of the negative plate, T is the temperature, F is the Faraday's constant, R is the molar gas constant, α is the transfer coefficient, I_0 is the exchange current and I_d is the diffusion current. The equation fits well the experimental data. A value of 4.3×10^{-6} A was obtained for the exchange current I_0 , the calculated transfer coefficient α was 0.06, and the diffusion current I_d was 0.423 A. The good correlation between the experimental data and the proposed fit identifies that O_2 recombination proceeds mainly according to the electrochemical mechanism (Eqn. 1). The obtained low value of the exchange current is typical for the $\text{H}_2\text{O}/\text{O}_2$ electrode, which is a strongly irreversible electrochemical system. The obtained unusually low value of the charge transfer coefficient means that the potential barrier is strongly shifted towards the products of the recombination reaction, i.e. the electrode surface. We could not find any data in the literature about the kinetic parameters of the O_2 recombination reaction on a Pb electrode.

The contribution of the recombination process to the total current flowing through the cell can be calculated from the $I_{\text{ECR}}(\varphi_-)$ dependence:

$$\eta_{\text{ECR}}(\varphi_-) = (I_{\text{ECR}} / I_{83\%}) * 100 \quad (4)$$

η_{ECR} will be denoted as the electrochemical efficiency of the COC.

The gassing current was calculated from the measured gas flow rate during the voltammetric sweep (Fig. 2a). The values of the gassing current were plotted vs. the same potential in Fig. 3a. Based on this curve the total efficiency of the COC (η_{TOT}) can be calculated:

$$\eta_{TOT} (\varphi_-) = 100 * (I_{83\%} - I_{gas}) / I_{83\%} \quad (5)$$

The total efficiency of the COC accounts for all possible mechanisms by which a water loss reduction is carried out. Both types of COC efficiencies are compared in Fig. 3b. As evident from the figure, there is but a minimum difference. This means that at 15°C an electrochemical mechanism is preferred during the COC operation.

3.2. Dependence of the rate of the overcharge processes on the potential taking place at the negative plate determined at 50°C.

Figure 4a illustrates the I / φ dependence at 50°C for two electrolyte saturation levels. At saturation 83% the shape of the curve and the current values are very similar to this recorded at 15°C (Fig. 2a) whereas at 100% saturation the current has increased substantially compared to Fig. 2a. This means that the electrochemical recombination current decreases with the negative plate potential increase. A substantial difference between both COC efficiencies is observed in Fig. 5b. This difference increases with the potential. The total efficiency remains high.

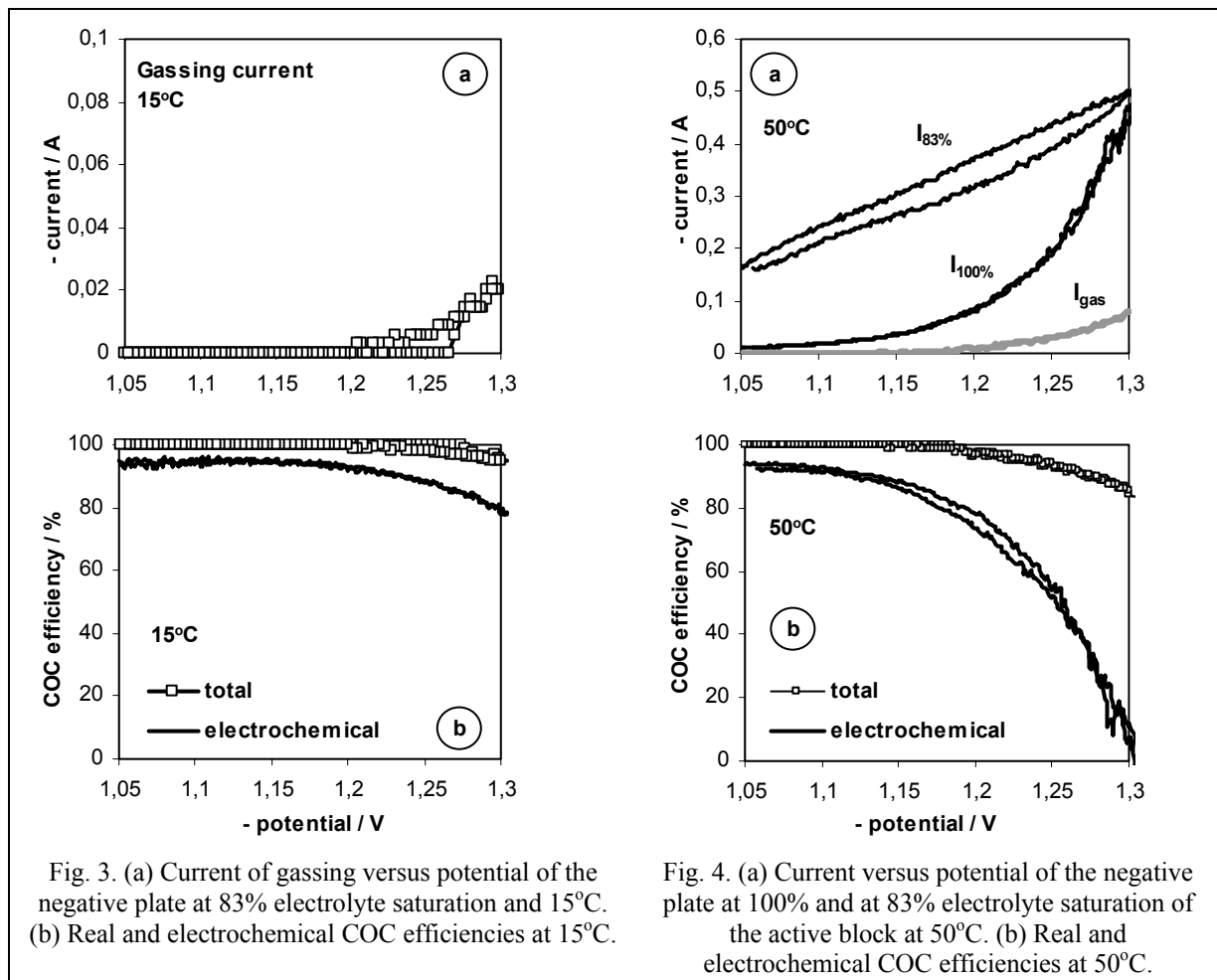
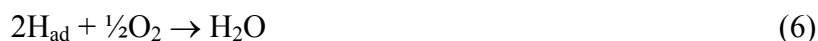


Fig. 3. (a) Current of gassing versus potential of the negative plate at 83% electrolyte saturation and 15°C. (b) Real and electrochemical COC efficiencies at 15°C.

Fig. 4. (a) Current versus potential of the negative plate at 100% and at 83% electrolyte saturation of the active block at 50°C. (b) Real and electrochemical COC efficiencies at 50°C.

What could be the reason for the increasing difference between the full and the electrochemical efficiency of the COC? The answer must be related to the ways in which

hydrogen evolved on the negative plate can react. It is known that hydrogen evolution is a one electron reaction – the adsorbed on the lead surface hydrogen atoms (H_{ad}) are formed initially and are further involved into chemical or electrochemical reactions leading to the formation of H_2 molecules. The latter can move towards the positive plate surface and oxidize their electrochemically. The rate of this process, however, is rather small [14-16]. Thus, the only remaining possibility is that a chemical reaction between the H_{ad} atoms on the lead surface and oxygen coming from the electrolyte proceeds in the following manner:



Similar oxygen recombination mechanism has been recently proposed by Guo *et al.* [17].

4. Conclusions

A new method was proposed to study the steady state dependence of O_2 recombination and COC efficiency on the potential of the negative plate. The method combines cyclic voltammetry and gas flow measurement. At temperatures below 20°C the electrochemical mechanism of O_2 recombination is the preferred reaction path of COC operation. At higher temperatures, a substantial part of O_2 recombination proceeds via a chemical reaction path. H_{ad} atoms react with and O_2 molecules to form water.

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