

Short communication

# Influence of temperature and electrolyte saturation on rate and efficiency of oxygen cycle in VRLAB

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## Abstract

The paper discloses the influence of the temperature and electrolyte saturation of the active block (positive and negative plates and AGM separator) on the rate and efficiency of the oxygen cycle (OC) in valve-regulated lead-acid batteries (VRLAB).

Applying steady-state cyclic linear sweep voltammetry and measuring the gas flow leaving the cell, the rate and efficiency of OC were measured at constant temperature and electrolyte saturation as a function of the negative plate potential. The obtained results show that at constant potential of the negative plate the rate of the OC depends slightly on temperature. However, the efficiency of the OC strongly depends on the temperature—the higher the temperature, the lower the OC efficiency.

The experimental results for the influence of the electrolyte saturation on the rate and efficiency of the oxygen cycle show that the saturation is the main rate- and efficiency-limiting factor. Combining the gas diffusion approach, porosimetric analysis of the NAM and AGM separator and the recently proposed model of the reactions that take place during the operation of OC, the mechanism of the influence of the electrolyte saturation on the rate and efficiency of the oxygen cycle was elucidated. It was shown that the optimal saturation value is about 93%.

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**Keywords:** Valve-regulated lead-acid batteries (VRLAB); Oxygen cycle; AGM separator; Electrolyte saturation; Temperature dependence; Oxygen recombination

## 1. Introduction

The main problem in the operation of the lead-acid batteries is the requirement for maintenance. In the valve-regulated lead-acid batteries (VRLAB) with absorptive glass mat (AGM) separator this problem is solved by an operation of an internal oxygen cycle (OC). When the state of charge (SOC) exceeds 70%, the oxygen is evolved on the positive plate, then passes through gas channels in the AGM separator, reaches the surface of the negative plate, and finally reacts chemically and/or electrochemically forming water. The channels through the AGM are formed due to the partial filling of the separator with electrolyte. The reduction of

oxygen on the negative plate is limited by two steps: diffusion of oxygen through a wetting electrolyte film, formed in the pores of the negative active mass (NAM) and impeded charge transfer during the electrochemical reactions on the lead surface [1–4]. The mechanism of the reactions taking place during the oxygen cycle operation at the surface of the negative plate of VRLAB is described in [5]. A scheme of these reactions is shown in Fig. 1.

The major factors limiting the rate of the reactions included in Fig. 1 are the negative plate polarization, temperature and electrolyte saturation of the active block. The negative plate polarization is directly related to the charge voltage of the battery. It influences the rates of the electrochemical reactions (1a, b and 2a). Recent studies show, that rising of the temperature leads to a decrease of the oxygen cycle efficiency [6]. On the other hand, decrease of the active block electrolyte saturation increases the rate of the reactions involved in the oxygen cycle and therefore increases the OC

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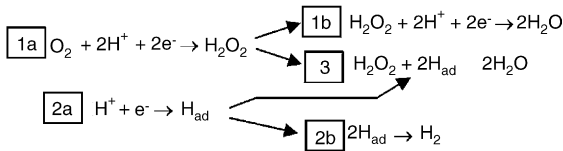


Fig. 1. Scheme of the oxygen cycle reactions involved in the reduction of oxygen and the evolution of hydrogen as well as in the chemical and electrochemical mechanisms of water formation at the negative plate [5].

efficiency [7,8]. As higher the oxygen cycle efficiency as lower the water loss in the system. The major problem in the above phenomenon is that during the operation of the oxygen cycle, the electrical energy, consumed by the battery for overcharging, is fully converted into heat [9]. At constant voltage charge the evolved heat increases the cell temperature, which may cause next autocatalytic rise of the charge current and subsequent additional increase of the cell temperature [9]. The phenomenon is well known as thermal runaway. The aims of the present work are to study the influence of the temperature and electrolyte saturation on the rate and efficiency of the oxygen cycle at different potentials of the negative plate and to find the optimum values of these parameters for the proper exploitation of VRLAB.

## 2. Experimental

### 2.1. Cell and experimental conditions

Experimental VRLA cells were assembled comprising two positive and one negative (1.5 Ah) plates separated by AGM separators (H&V, 440 g m<sup>-2</sup>, BCI thickness 2.6 mm) and a Hg/Hg<sub>2</sub>SO<sub>4</sub> reference electrode. The pore size distribution of the AGM separator was characterized by capillary flow porometer (PMI, Porous Materials, Inc.). Fig. 2 represents the scheme of the experimental setup. The dimensions

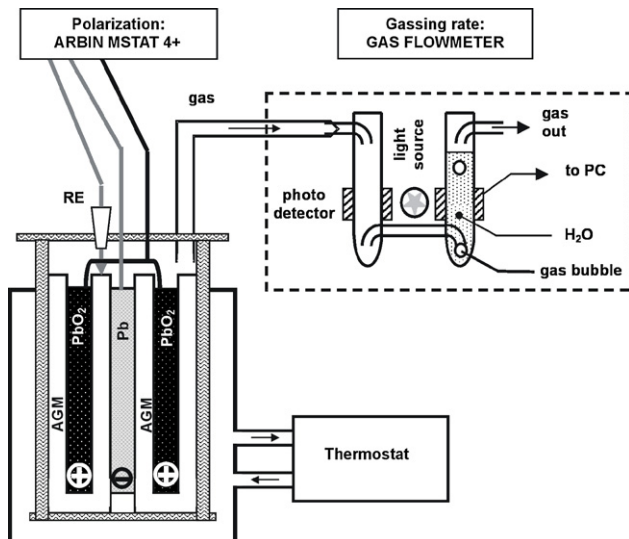


Fig. 2. Scheme of the experimental setup.

of the plates were 1.7 mm × 60 mm × 51 mm and the grid alloy was Pb–1%Sn–0.1%Ca. All plates were tank-formed and dry charged. The active block was assembled with 15% compression of the AGM separators. The negative plate was the working electrode, while the positive plates were counter-electrodes and oxygen sources.

The cells were flooded with sulfuric acid solution with s.g. 1.27 and left to soak for 30 min. Then the excess electrolyte was removed. The cells were connected to a potentiostat/galvanostat MSTAT4+ (ARBIN Instruments). First, they were conditioned by imposing 10 charge–discharge cycles, at 100% electrolyte saturation, employing the following program: discharge at 300 mA until the potential of the negative plate reached  $\varphi^- = -0.7$  V (versus Hg/Hg<sub>2</sub>SO<sub>4</sub> ref. electrode), charge at 300 mA until charge factor (FC) goes to 105% and further charge at 150 mA until FC = 125%. After the initial cycling the cells were set only to overcharge. The electrolyte saturation of the active block was controlled by the cell weight and varied between 83 and 100% by a constant current overcharge. The kinetics of the process of oxygen recombination was investigated through linear sweep voltammetry (LSV) from –1.05 to –1.30 V at potential scan rate 0.02 mV s<sup>-1</sup>. All individual experiments were performed at constant temperature and the investigated temperature range was from 15 to 60 °C (±0.1 °C). The rate of the gas flow leaving the cells was measured continuously by a flowmeter (designed as presented in [6]) and re-calculated in current units.

After the polarization experiments samples from the negative active mass was washed, dried in nitrogen atmosphere and analyzed by X-ray diffraction (APD 15, PHILIPS) and mercury porosimetry (Auto pore 9200, MICROMERITICS). The volume fraction of Pb, determined from the XRD data, was higher than 96%.

### 2.2. Oxygen cycle current and efficiency

In the beginning of the experiment the cells were fully charged. Therefore, the main reactions that took place at the positive and negative plates were water decomposition to oxygen and reduction of oxygen with a formation of water and H<sub>2</sub> evolution. The corrosion rate of the positive grids was ignored.

When the charged cells were set to overcharge, reactions of chemical and electrochemical reduction of oxygen and decomposition of water with evolution of hydrogen take place at the negative plates. The rates of these reactions can be represented by the respective currents. The oxygen cycle current,  $I_{OC}$ , depends on all mechanisms of oxygen reduction during the oxygen cycle operation and is determined by the equation:

$$I_{OC} = I_{np} - I \quad (1)$$

where  $I_{np}$  is the current at the negative plate and  $I$  is the current due to the reaction (2a) (see Fig. 1).  $I$  is calculated from the gas flow leaving the cell, where the gas is a stoichiometric

mixture of oxygen and H<sub>2</sub> with volume ratio 1:2. The efficiency of the oxygen cycle ( $\eta_{OC}$ ) can be determined by the formula:

$$\eta_{OC} = \frac{100 I_{OC}}{I_{np}} \quad (2)$$

### 3. Results and discussion

#### 3.1. Temperature dependence of the oxygen cycle rate

The dependence of the oxygen cycle rate on the temperature was studied at 83% electrolyte saturation of the active block. The results are shown in Fig. 3. The curves correspond to different values of the negative plate potential. It is seen from the graph that the temperature does not affect the oxygen cycle rate and the Arrhenius law is not valid.

The first step of the oxygen cycle is reaction (1a) (see Fig. 1). The open circuit potential of the negative plate ( $-0.98$  V versus Hg/Hg<sub>2</sub>SO<sub>4</sub>) is much lower than the equilibrium potentials of the electrodes O<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>/H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O (which are, respectively, +0.05, +0.58 and +1.12 V).

Hence, the major limits for the oxygen cycle reactions are the solubility and diffusion of the oxygen in the electrolyte. When the temperature increases, the solubility of the oxygen in the electrolyte decreases causing a decrease of the oxygen flow within the wetting film. At the same time, the increase of the temperature leads to an increase of the value of the diffusion coefficient of oxygen in the electrolyte and accelerates the process of oxygen diffusion through the wetting film. The effects of the temperature on solubility and diffusion of oxygen are opposite and may lead to a compensation of both factors as it is shown in Fig. 3. At fixed values of the negative plate potential the rate of the oxygen cycle does not depend on the temperature for the whole range of  $T$  in the experiment (see Fig. 3).

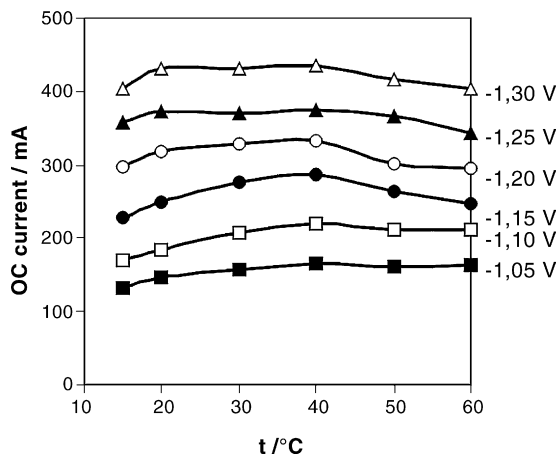


Fig. 3. Temperature dependence of the oxygen cycle current at 83% electrolyte saturation of the active block.

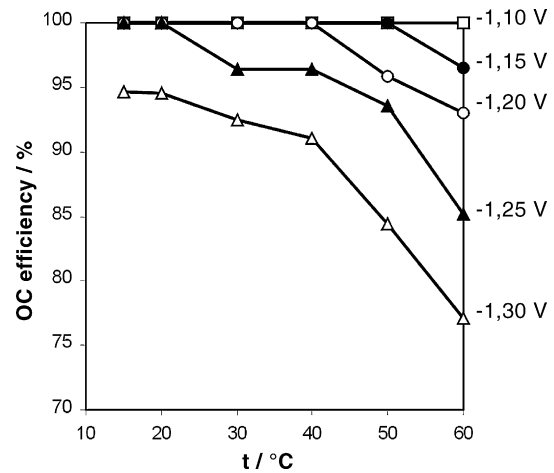


Fig. 4. Temperature dependence of the oxygen cycle efficiency at 83% electrolyte saturation of the negative plate.

#### 3.2. Temperature dependence of the oxygen cycle efficiency

The efficiency of the oxygen cycle was calculated from the data shown in Fig. 3 using Eq. (2). Its dependence on the temperature is plotted on Fig. 4. For all potentials  $\varphi^-$  higher than  $-1.10$  V the efficiency is 100% and does not depend on the temperature. When  $\varphi^-$  becomes lower than  $-1.15$  V, the oxygen cycle efficiency shows strong dependence on the temperature. With increasing of the absolute value of the negative plate potential,  $\varphi^-$ , the temperature until which the system operates at 100% efficiency decreases. For example, for  $\varphi^- = -1.20$  V the oxygen cycle efficiency is 100% for  $t < 40$  °C, while for  $\varphi^- = -1.30$  V the efficiency is 95% even at 15 °C (see Fig. 4). These values are critical for the proper operation of the VRLAB. If the oxygen cycle efficiency decreases the cell loses water and the life of the battery becomes shorter.

The above data can be explained by the mechanism presented in Fig. 1. When the temperature of the cell increases, the hydrogen overvoltage decreases. This leads to an increase of the rate of the reaction (2a). At the same time, the overall rate of water formation does not depend substantially on the temperature (see Fig. 3) and the rates of the other reactions do not change. Hence, the rate of H<sub>2</sub> formation increases and efficiency of the oxygen cycle decreases. The negative plate potential influences the oxygen cycle efficiency on the same way. When the negative plate is cathodically polarized the rate of the reaction (1a) tends to its diffusion limiting value. The rate of reaction (2a) rises according to the Tafel equation and the adsorption of H<sub>ad</sub> atoms increases. This leads to the formation of more H<sub>2</sub> molecules and further decrease of the oxygen cycle efficiency. On the other hand the rate of reaction (3) rises but this process does not change the overall rate of oxygen reduction. It changes only the ratio between the rates of reactions (1b and 3), because the flow of oxygen towards the lead sur-

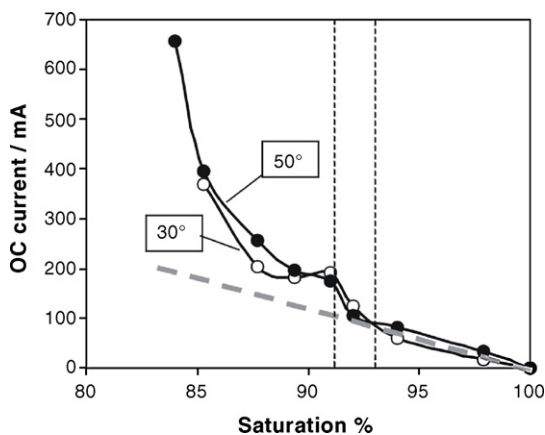


Fig. 5. Dependence of the oxygen cycle current on the electrolyte saturation at  $\varphi^- = -1.20$  V and 30 and 50 °C.

face is diffusion limited and the rate of reaction (1a) remains constant.

### 3.3. Influence of the electrolyte saturation on the rate of the oxygen cycle

The dependence of the oxygen cycle current on the electrolyte saturation of the active block at  $\varphi^- = -1.20$  V and two different temperatures is plotted in Fig. 5. The obtained results show very slight effect of the temperature for the whole range of the electrolyte saturation studied. When the saturation is higher than 93% the dependence is close to linear. This means that in this region the rate of the oxygen cycle is limited by the saturation of the AGM.

At high saturations, the active surface area at which the oxygen cycle reactions take place is localized close to the AGM/NAM interface and is proportional to the AGM saturation. Such assumption can be supported by the comparison of the pore-size distributions of the AGM and NAM, shown in Fig. 6a. Since the amount of the electrolyte in the AGM is much bigger than those in the pores of NAM it can be assumed that the electrolyte saturation of the active block is equal to the saturation of the AGM. When the AGM saturation is about 93%, the saturation of NAM is about 70% (see Fig. 6a). At this saturation of NAM only the macro-pores of the plate are filled with gas. Fig. 6b shows that these pores have relatively small surface area. Hence, the contribution of the gas-filled macro-pores to the overall rate of the oxygen cycle is small. So, the rate of the process is limited by the saturation of the AGM.

When the saturation of the active block becomes lower than 93%, the oxygen cycle rate increases exponentially. Only the increase of the number of the gas channels through the AGM cannot explain this result. Hence, for the explanation of this effect we have to look at the processes that take place at the NAM. It was shown [4] that the main limiting step for the oxygen cycle is the diffusion of oxygen through the

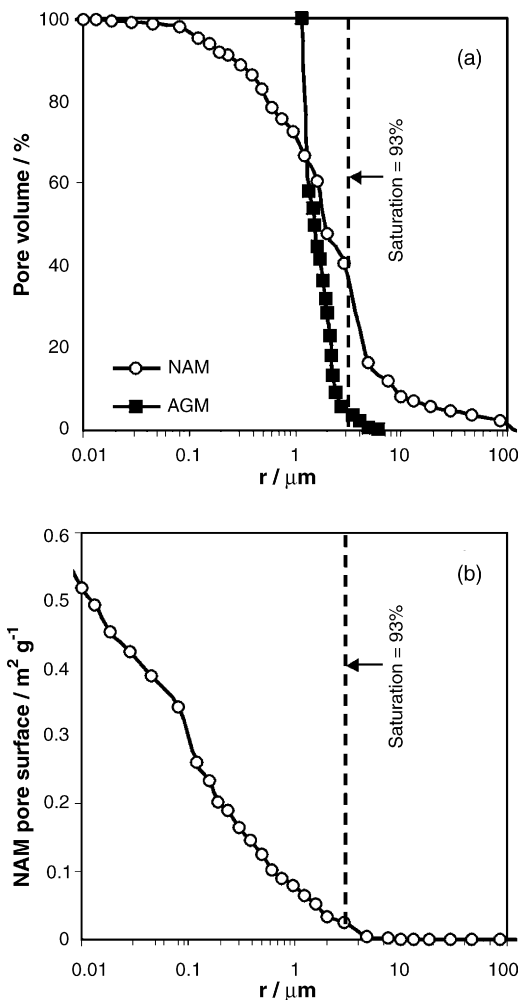


Fig. 6. (a) Cumulative pore volume as a function of the pore radius for NAM and AGM and (b) pore surface as a function of the pore radius for NAM. The dotted line notes 93% electrolyte saturation of the active block.

wetting electrolyte film in the pores of NAM. So, at constant temperature and negative plate potential the decrease in the saturation of NAM will change the surface area and thickness of the wetting films as well as the electrolyte concentration. The area of the wetting films is proportional to the surface of the gas-filled NAM pores. The dependence of the area of the pores filled with gas on the NAM saturation was calculated from the mercury porosimetric data (Fig. 6a and b). The results are presented on Fig. 7. It can be seen from the graph that when the negative plate saturation becomes lower than 70–80% the area of the gas-filled pores increases exponentially. Therefore, the exponential increase of the OC rate at low saturations (Fig. 5) can be attributed to the increase of the area of the gas-filled pores in NAM and the processes taking place there.

The diffusion length at the oxygen reduction process coincides with the thickness of the wetting film. According to the gas-diffusion approach explained in [4] the thickness of the wetting film depend on the radius of the gas-filled NAM pore.

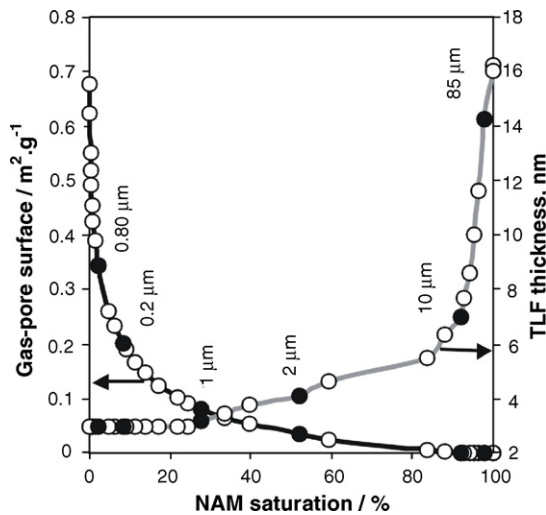


Fig. 7. Dependence of the area of the gas-filled NAM pores (black curve) and wetting film thickness (gray curve) on the electrolyte saturation of NAM. The black dots correspond to the listed pore radii.

The dependence is given by the equation:

$$h = \left( \frac{3 \times 10^{-13} r}{4\pi\sigma} \right)^{1/3} \quad (3)$$

where  $r$  is the radius of the gas-filled NAM pore and  $\sigma$  is the surface tension of the gas/electrolyte interface. The value of  $\sigma$  used for calculation of  $h$  was assumed to be  $70 \text{ mN m}^{-1}$ . By using the dependence of the pore volume on  $r$  the results for  $h$  are presented as a function of NAM saturation (see Fig. 7). It is seen that with decreasing of the NAM saturation the thickness of the wetting films also decreases. The limiting value of 3 nm corresponds to the thickness of the two adsorption monolayers of lignin molecules on the wetting film interfaces [10].

### 3.4. Influence of the electrolyte saturation on the efficiency of the oxygen cycle

Fig. 8 shows the efficiency of the oxygen cycle on the electrolyte saturation at  $\phi^- = -1.20 \text{ V}$ . The two curves correspond to  $T = 30^\circ\text{C}$  and  $50^\circ\text{C}$ . When the active block saturation becomes higher than 93%, the efficiency of the oxygen cycle sharply decreases. Below this value, the efficiency is higher than 85% and tends to 100%. Thus, when the saturation is about 93% the operation of the oxygen cycle is optimal. First, the rate of the oxygen cycle is low enough to keep the cell temperature at low level. Second, depending on temperature, the efficiency of the oxygen cycle tends or reaches its maximum value and the water loss is avoided.

The data in Fig. 8 can be explained by the mechanism shown in Fig. 1. At constant temperature and negative plate potential the rate of the reactions in Fig. 1 are determined by the electrolyte saturation of the active block. The dependence of the electrolyte density on the saturation in the range 100–83% can be neglected (electrolyte density is  $1.27 \text{ g cm}^{-3}$

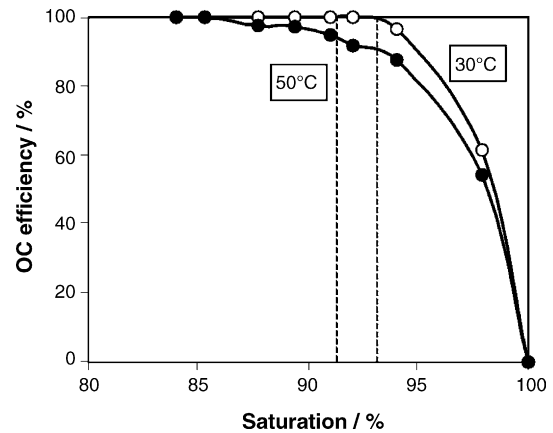


Fig. 8. Dependence of the efficiency of the oxygen cycle on the electrolyte saturation of the active block at  $\phi^- = -1.20 \text{ V}$  and 30 and  $50^\circ\text{C}$ .

at 100% saturation and  $1.335 \text{ g cm}^{-3}$  at 83% saturation). The saturation does not affect the rate of the hydrogen evolution (reaction (2a)). On the same time when the saturation increases the rate of the reaction (1a) decreases. Therefore, at high saturation the hydrogen evolution will dominate other processes, which will lead to decrease of the rate of the oxygen reduction and subsequently to decrease of the OC efficiency. The results for the rate an efficiency of the oxygen cycle (see Figs. 5 and 8) show that the optimal saturation level of the active block is around 93%.

## 4. Conclusions

In the present work, we study the influence of the temperature and the saturation of the active block on the rate and efficiency of the oxygen cycle. The results show that at constant negative plate potential the temperature does not affect the rate of the OC. The effect is explained by the gas-diffusion approach, which shows that the two limiting factors, oxygen diffusion and oxygen solubility in the wetting film, act in opposite directions and cancel each other. The effect of the temperature on the efficiency of OC is quite dramatic. The increase of the temperature leads to an increase of the rate of  $\text{H}_2$  formation and subsequently to a rapid decrease of the oxygen cycle efficiency. The decrease of the negative plate potential strengthens the effect. This explains the short exploitation period of VRLAB at higher temperatures.

The experimental results for the influence of the electrolyte saturation of the active block on the rate and efficiency of the oxygen cycle show that the saturation is the main rate- and efficiency-limiting factor. Combining the gas diffusion approach and porosimetric analysis of the NAM and AGM separator a mechanism for influence of the active block electrolyte saturation on the rate of the oxygen cycle was proposed. It was shown that the optimal saturation value is about 93%. The obtained results are in agreement with recently proposed model [5] for the mechanism of the reactions of oxygen

reduction with the participation of hydrogen, that take place on the negative plate.

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