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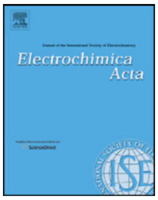

Oxygen evolution on alpha-lead dioxide electrodes in methanesulfonic acid

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ABSTRACT

This work examines the oxygen evolution reaction (OER) taking place on α-PbO_2 electrode in methanesulfonic acid (MSA) medium and in sulphuric acid as a comparison, by means of cyclic voltammetry (CVA) and electrochemical impedance spectroscopy (EIS), for soluble lead acid flow battery applications. The influence of MSA concentration on OER is studied. EIS measurements highlighted the impact of the hydrated lead dioxide layer upon decreasing MSA or sulphuric acid concentration. The evolution of the Tafel curves plotted from EIS measurements and quasi-stationary currents while varying acid concentration was interpreted in the light of this hydrated layer which could enhance the electrocatalytic activity when it is thin, and on the contrary act as an electronic barrier when growing for low acid concentration. Both EIS and CVA revealed that OER on lead dioxide is less favoured in MSA than in sulphuric acid. It is finally concluded that a high-concentrated MSA electrolyte is better for lead acid flow battery application in terms of oxygen evolution.

1. Introduction

A new type of redox flow battery, based on lead(II) dissolved in the electrolyte, was recently proposed by Pletcher et al. in a series of papers [1–10]. This soluble lead flow battery (SLFB) works with a single electrolyte made up of methanesulfonic acid (MSA, formula: CH_3SO_3H) which contains dissolved lead(II) ions in the form of $Pb(CH_3SO_3)_2$. The reactor consists of two electrodes between which flows the electrolyte. Lead(II) is oxidised into lead dioxide at the positive electrode and reduced into lead at the negative during charge. During discharge, PbO_2 and Pb turn back to Pb(II) in solution in MSA. The overall battery reaction is:

$$2Pb^{2+} + 2H_2O \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} PbO_2 + Pb + 4H^+$$

The lead(II) concentration in the electrolyte decreases when the battery is charged. In the same time, the protons concentration increases twice as fast.

The system differs from traditional lead acid batteries in that the electrolyte contains the active soluble lead(II) species, so that there is no solid phase reaction. The main advantage of this technology compared to other redox flow systems is that no membrane or separator is required since the electrolyte is the same for both electrodes. In addition, methanesulfonic acid is a less hazardous and more environmentally friendly electrolyte than other acids [11].

Oxygen evolution reaction (OER) taking place at the positive electrode during charge leads to a decrease in the faradic efficiency of PbO_2 deposition, and hence leads to losses in energy efficiency and chemical imbalance at the two electrodes (excess of lead at the negative electrode) [6]. Moreover, it has been established [12] that uniform and well-adherent PbO_2 layers are deposited from MSA electrolyte in low current density and low temperature conditions, whereas powdery or pitted PbO_2 of poor adhesion are obtained using a high current density and/or high temperature, i.e. conditions favouring O_2 evolution. It is highly possible that O_2 evolution play a significant role in the loss of PbO_2 in the form of small particles in the electrolyte during SLFB cycling encountered by Pletcher's team [10]. Therefore studying oxygen evolution reaction on lead dioxide material in methanesulfonic acid medium appeared to be worthwhile.

While there is quite a lot of the literature concerning oxygen evolution on PbO_2 material in several electrolytes like H_2SO_4 [13–24], $HClO_4$ [15,22], H_3PO_4 [15], or CF_3SO_3H [21], no OER investigation on PbO_2 was carried out in methanesulfonic acid, probably due to its recent application in lead acid batteries technology.

The general mechanism leading to O_2 formation can be written as:

$$H_2O \rightarrow OH^{\bullet}{}_{ads} + H^+ + e^- \tag{1}$$

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$$OH^\bullet \rightarrow O_{ads} + H^+ + e^- \quad (2)$$

followed by the chemical recombination of oxygen:

$$2O_{ads} \rightarrow O_2 \quad (3)$$

Pavlov et al. [17,18] proposed that this mechanism take place on active centers $PbO(OH)_2$ located in a hydrated lead dioxide layer at the PbO_2/electrolyte interface according to:

$$PbO(OH)_2 + H_2O \rightarrow PbO*(OH)_2 \ldots OH^\bullet + H^+ + e^- \quad (4)$$

$$PbO(OH)_2 \ldots OH^\bullet \rightarrow PbO*(OH)_2 + O_{ads} + H^+ + e^- \quad (5)$$

$$2O_{ads} \rightarrow O_2$$

The kinetics of OER studied by steady-state polarization (current density vs. electrode potential), and represented by the slopes of the *E*. vs. log*j* plots (Tafel coefficient *b*), depends to a great extent on PbO_2 structure (i.e. on the deposition conditions) [19,24] and allotropic form (α or β) [14,16]. The most commonly encountered *b* value is 120 mV [15,16,19,22], which corresponds to a single electron transfer reaction with a α transfer coefficient of 0.5 ($b = \ln 10 \times RT/\alpha zF$) at 25 °C. But values as high as 277 mV [24], or 344 mV [23] can be found.

The relative kinetics of the two electrochemical reactions is still not clear. Da Silva et al. [25] proposed that the primary water discharge (1) be the rate determining step (r.d.s.), Ho et al. [16] invoke the oxidation of adsorbed $OH^\bullet$ as r.d.s.

The present paper is dedicated to the study of O_2 evolution on lead dioxide in methanesulfonic acid medium. Cyclic voltammetry was first used to calculate the kinetic parameters (Tafel coefficient and activation energy). Then electrochemical impedance spectroscopy was employed for further investigations on the reaction mechanisms. The lead dioxide allotropic form α was chosen because of its recognition by Pletcher et al. [7] to be the most convenient form for SLFB application due to its compact and well-adherent structure.

2. Experimental

2.1. PbO_2 deposition conditions

The disc electrodes on which lead dioxide was deposited were made up of a glassy carbon rod (diameter ~0.3 cm, cross-section ~0.071 cm^2) embedded in Plexiglas tubes filled with epoxy resin. Before each deposition, the glassy carbon surface was pre-treated by anodic etching, subjecting the electrode to a constant anodic current (30 mA cm^{-2}) in 1 M NaOH during 10 min, in order to improve PbO_2 adhesion due to glassy carbon roughening [26].

α-PbO_2 (250 μm thick) was electrodeposited onto glassy carbon electrode at room temperature from a 1 M $Pb(CH_3SO_3)_2$ + 0.2 M CH_3SO_3H + 5 mM $C_{16}H_{33}(CH_3)_3N^+$ solution prepared by adding PbO (99%, *Sigma–Aldrich*) and hexadecyltrimethylammonium p-toluene sulfonate ($C_{16}H_{33}(CH_3)_3N{\cdot}C_7H_6SO_3H$, 99%, Sigma–Aldrich) to a methanesulfonic acid solution (from MSA 70%, *Alfa Aesar*). $C_{16}H_{33}(CH_3)_3N^+$ cation was used by Pletcher et al. [5] to improve lead deposition quality in their redox flow battery (5 mM in electrolyte). The electrodeposition was performed with a constant anodic current of 50 mA cm^{-2} for 1 h, according to a protocol derived from Sirés et al. [12] for electrodeposition of uniform and well-adherent α-PbO_2 layer, using a Pt counter-electrode.

2.2. Cyclic voltammetry and electrochemical impedance spectroscopy

Oxygen evolution on α-PbO_2 was studied using cyclic voltammetry (CVA) and electrochemical impedance spectroscopy (EIS) in methanesulfonic acid at different concentrations (from 0.25 to 5 M), and in sulphuric acid as a comparison. All measurements were performed using a classical 3-electrode cell (working PbO_2 electrode, Pt counter electrode, reference electrode) with a homemade Ag/Ag_2SO_4 reference electrode (E = 0.654 V/SHE). The solutions were all magnetically stirred to remove the bubbles from the electrode surface as much as possible, and to be closed to the electrolyte flowing conditions of the battery. Such convection is not expected to have an influence on the kinetics of the reaction because oxygen evolution reaction comes from water which is the solvent. In these conditions, the rate of the process is not expected to be diffusion controlled (no depletion in water molecules can happen near the electrode surface for there are in strong excess) but only kinetically controlled by the reaction itself. Thus the convection will not have any strong effect both on the polarization curves and on the EIS diagrams, which reflect the kinetics of the reaction.

CVA measurements was carried out recording four potential cycles under quasi-stationary conditions (potential scan rate 0.5 mV s^{-1}), from 1.1 V to 1.3 V, after a 30 min constant polarization step at 1.1 V, for different temperatures (25–65 °C, with 10 °C-increments). Tafel curves (*E* vs. log*j*) were plotted for the anodic sweep of the last cycle, while Arrhenius curves (log*j* vs. 1/*T*) for potentials ranging from 1.1 to 1.3 V were obtained calculating the average current value on the anodic sweep over the four cycles for each potential and temperature.

EIS consisted in applying a sinusoidal potential (amplitude: 5 mV, frequency range: 5 mHz–65 kHz) added to different d.c. potentials ranging from 1.1 to 1.4 V (25 mV-increments) to the PbO_2 electrode. Before each impedance measurement at a given d.c. potential, the electrode was polarized at this potential during 15 min to make sure that the current remained stable and that bubbles formation and detachment had no incidence on the impedance of the electrode. All EIS measurements were performed at 25 °C.

2.3. Instrumental

Carbon etching, PbO_2 deposition, and cyclic voltammetry were all performed using a *Solartron 1470* apparatus monitored by *CorrWare*. XRD analysis and SEM images were carried out respectively on a *Brücker D8 Advance* diffractometer and a *FEI Nova NanoSEM 630* scanning electron microscope. EIS measurements were performed with a *Solartron SI 1250* monitored by *Zplot*. EIS data treatments (Nyquist diagrams fitting with equivalent circuits) was done with *ZView 2* software, and extracted capacities calculated with *Matlab*. Cell's temperature was regulated with a *Bioblock Scientific* thermostat.

3. Results and discussion

3.1. Voltammograms, Tafel and Arrhenius plots

A X-ray diffractogram and SEM images of a PbO_2 coating deposited in the conditions described in Section 2.1. are shown in Fig. 1. The identification of the diffraction peaks was done using the PDF-2 database from ICDD. Most of the peaks can be identified to the α form of PbO_2, while very few peaks corresponding to the other allotropic form of lead dioxide (β-PbO_2) can be found. The fact that no significant peak exclusively associated to β-PbO_2 can be observed strongly indicates that the large majority of the lead dioxide coating is in the α (orthorhombic) form, as expected. The mean crystallite size, estimated using the Debye-Scherrer equation with the full width at half maximum (FWHM) of the (0 2 0) or (0 2 1) diffraction peak, was found to be around 15 nm, which is in good accordance with Sirés et al. [12] who reported a mean crystallite size of 13 nm for lead dioxide deposited in the same