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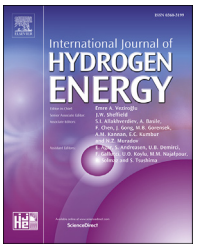

Study of methanesulfonic acid effect on electrosynthesis of lead dioxide to provide more environmentally electrolyte selection

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ABSTRACT

Lead dioxide has absorbed much attention for its good resistance to corrosion, high electronic conductivity, good stability, long lifetime, low cost as electrode material. However, there still exist problems about the selection of electrolyte, which may bring trouble in energy conservation and environmental protection. The present study was to provide more environmentally electrolyte of methanesulfonic acid (MSA) and evaluate MSA effect on electrosynthesis of lead dioxide by using rotating disk electrode (RDE) and scanning electron microscope (SEM) as well as X-ray diffraction (XRD) so as to make sure suitable concentration of MSA and to gain more environmental and energy benefit. The results show that methanesulfonic acid has great influence on the electrodeposition of lead dioxide and adequately characterise the PbO_2 synthesized on Pt electrode surface. By controlling the composition of the electrodeposition bath at MSA concentration 0.1 M and Pb(II) 0.2 M can we get better reversible process, longer electrode lifetime and more satisfactory environmental protection.

Introduction

Zinc is mainly extracted from its sulfide ores, oxide ores or other secondary resources by means of electrowinning process for hydrometallurgy, during which, lead dioxide (PbO_2), as the electrode material, is extremely attractive due to its good resistance to corrosion, high electronic conductivity, good stability in acidic media, long lifetime, low cost, and high overpotential for oxygen evolution compared with other materials [1–10]. During the electrowinning process, prominent problems that arise are about the selection of electrolyte, which may bring trouble in energy conservation and environmental protection. Traditional process are processed by using alkali or acid solution [11–13], as well as the waste may result in various extent damages to the environment. Selecting appropriate electrolyte and suitable composition of the electrodeposition bath can not be ignored.

Methanesulfonic acid (MSA), as an environmentally friendly electrolyte, has been considered to be used in metal finishing industry as for its chemical stability, high ion conductivity, biodegradability and low toxicity [14–17]. However, most of the

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studies are focused on the application to undivided, soluble lead-acid flow batteries, researches of gaining stable PbO_2 electrodeposits by controlling environmentally concentration of MSA are scarce [18–20]. Alexandre Oury and co-workers have focused on studies of the electrodeposition cycling of lead dioxide (PbO_2) on vitreous carbon electrodes in lead methanesulfonate for a soluble lead acid flow battery application. They pay much attention to the study of the concentration in lead(II) in electrolyte to make sure its longest life [21,22]. Velichenko et al., who focused on the nucleation and growth mechanism of PbO_2, concludes that the current efficiency increases at higher temperature and Pb(II) concentration and at lower MSA concentration [23,24]. Compared to classical acidic media, the presence of methanesulfonate ions yields a higher deposition rate ending in thicker coatings without changing the mechanistic aspects [20,22]. It is then important to study the effect of MSA concentration on electrodeposition of lead dioxide by adequately characterizing the PbO_2 synthesized on Pt electrode surface to investigate more environmentally concentration of MSA in the electrowinning process.

The aim of this work is to study and carry out the effect of MSA on electrodeposition of lead dioxide, as well as to select environmentally concentration of MSA based on the maximum usage of energy. An alternative way to achieve this goal is to use the Koutechy-Levich equation to calculate the effect of MSA on diffusion coefficient D, as well as apparent heterogeneous rate constant k of the electrodeposition process and to express the relative contribution of mass transport and kinetics. The phase compositions and surface microstructures of deposits synthesized on the platinum surface can be respectively investigated by scanning electron microscope (SEM) and X-ray diffraction (XRD). Electrochemical characterisation by linear and cyclic voltammetry was also performed to study reactions and the electrochemical stability. The benefits gained from using methanesulfonic acid solutions in the study of electrochemical behaviour are illustrated, specifically when using a rotating disc electrode (RDE), which is a well-established experimental technique to study the mechanism of electrochemical reactions and to determine their kinetic parameters [25–33].

Experimentation

Apparent heterogeneous rate constant and diffusion coefficient

According to the Koutecky-Levich equation, it is available to calculate the values of the apparent heterogeneous rate constants (k) and diffusion coefficients (D) for Pb(II) oxidation from the linear plots of I^{-1} versus $\omega^{-1/2}$:

$$I^{-1} = \left(0.62nFAD^{2/3}\nu^{-1/6}C\omega^{1/2}\right)^{-1} + (nFAkC)^{-1} \quad (1)$$

where n is the effective number of electrons exchanged in the reaction, F the Faraday constant (C/mol), A the surface area of Pt-RDE (m^2), ν the kinematic viscosity of the solution (m^2/s), C the bulk concentration of the reacting species (mol/m^3) and ω the angular velocity of Pt-RDE (rad/s). Among which kinematic viscosity (ν) is calculated by the equation:

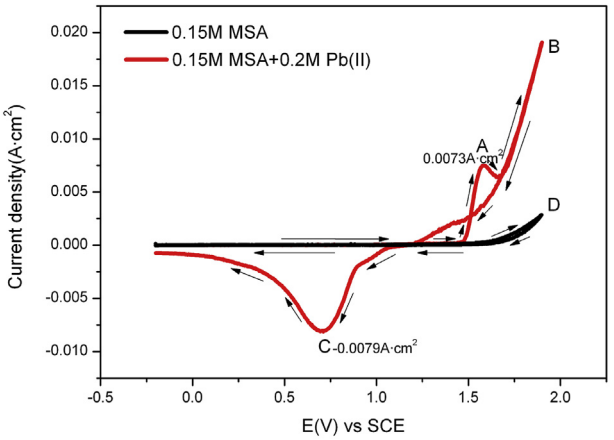

Fig. 1 – Cyclic voltammogram of a Pt electrode in 0.15 M MSA + 0.2 M Pb(II) solution, in comparison with a blank solution (scan rate, 50 mV/s).

$$\nu = \mu / \rho \quad (2)$$

where μ is the dynamic viscosity of the solution (Pa s) and is measured by Brookfield viscometer, ρ is the density of the solution (kg/m^3) that represents the ratio of mass and volume.

Physical and electrochemical characterization

The PbO_2 synthesized was examined by sensitive and widely used techniques for the chemical kinetics investigation of cyclic voltammetry and rotating disk electrode (RDE) voltammetry techniques. All cyclic voltammetry experiments were obtained using aqueous solutions of MSA and Pb(II) at different concentrations of room temperature. Galvanostatic deposition was carried out at a controlled MSA concentration, in the range of 0.05–0.2 M. Keep the Pb(II) concentration at 0.2 M during all experiments. The solution was equipped with the analytical grade reagents (AR) and twice-distilled water used for all solutions and high purity nitrogen gas into the solutions for 20 min before applying the potential. A Pt RDE (Ametek) with an exposed Pt area of 0.196 cm^2 mounted to a rotator, a platinum

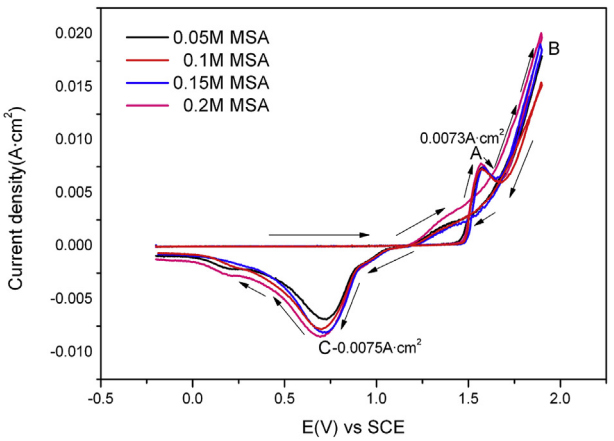

Fig. 2 – Cyclic voltammogram of a Pt electrode in solution of different MSA concentrations, Pb(II) controlled at 0.2 M (scan rate, 50 mV/s).

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