Electrochemical Noise Analysis of O_2 Evolution on PbO_2 and PbO_2-Matrix Composites

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Oxygen evolution is one of the most important and widely investigated electrochemical reactions, as it is the anodic process occurring during water electrolysis and, quite often, in metal electrodeposition. In recent years, oxide-matrix composites have been prepared by co-deposition of small particles (< 1 μm) of compounds like Co_3O_4 or RuO_2 with a PbO_2 matrix anodically generated by oxidation of Pb^{2+} ions[1,2]. These composites, in particular $PbO_2+Co_3O_4$, are active electrocatalysts for oxygen evolution from alkaline media, which exhibit stable performance during several days of continuous galvanostatic electrolysis. Besides introducing catalytically active centers, co-deposition of Co_3O_4 particles induces a marked increase of the PbO_2 matrix roughness; both phenomena contribute to shift the oxygen evolution reaction (*oer*) to lower overpotentials.

In the present communication we describe an investigation of the *oer* on both the pure PbO_2 matrix and $PbO_2+Co_3O_4$ composite oxides, carried out by electrochemical noise analysis. The evolution of oxygen bubbles has been investigated under galvanostatic regulation, by simultaneously measuring the fluctuations of both potential and electrolyte resistance. With this approach, purely ohmic effects could be measured and compared with the overall potential signals which contain both ohmic and non-ohmic (faradaic) contributions.

Figure 1 shows the power spectral densities (PSDs) of the electrolyte resistance $\Psi_{Re}(f)$, part A, and potential $\Psi_V(f)$, part B, induced by oxygen bubble evolution on either PbO_2 or $PbO_2+Co_3O_4$ working electrodes at a current density of 10 mA cm^{-2}. For both electrode materials $\Psi_{Re}(f)$ plots are almost identical, suggesting that the bubbles evolution profiles (i.e. the mean bubble size and their rate of departure) were very similar, in spite of the different surface conditions. In contrast, potential fluctuations gave rise to distinct PSDs, depending on the electrode material. For $PbO_2+Co_3O_4$, $\Psi_V(f)$ has the same general aspect as $\Psi_{Re}(f)$, indicating that potential fluctuations are mainly induced by ohmic effects, which is confirmed by the fact that $\Psi_V(f)$ is very close to the calculated ohmic-drop fluctuations, $\Psi_{Re,I}(f) = I^2.\Psi_{Re}(f)$, as seen in Fig. 2. On the other hand, in the case of the pure PbO_2 matrix, a plateau appears for $\Psi_V(f)$ at about 0.1 Hz, which must be ascribed to non-ohmic contributions, since no plateau was found in $\Psi_{Re}(f)$ plots. These non-ohmic contributions are not present in the case of composite electrodes and might be due to indirect effects of coalescence processes taking place to a different extent on the two types of electrodes.[3]

Further experiments are being carried out in order to interpret the behaviour of different electrode materials and elucidate the role of concentration of catalytically active centres and electrode roughness.
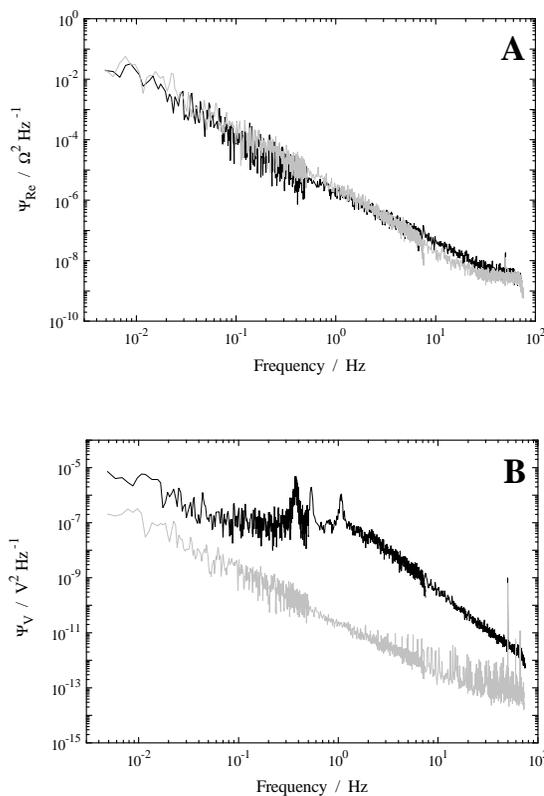

Figure 1. Power spectral densities of the electrolyte resistance $\Psi_{Re}(f)$, part A, and potential, $\Psi_V(f)$, part B, induced by the *oer* on either PbO_2 (black) or $PbO_2+Co_3O_4$ (gray) electrodes at 10 mA cm^{-2}.
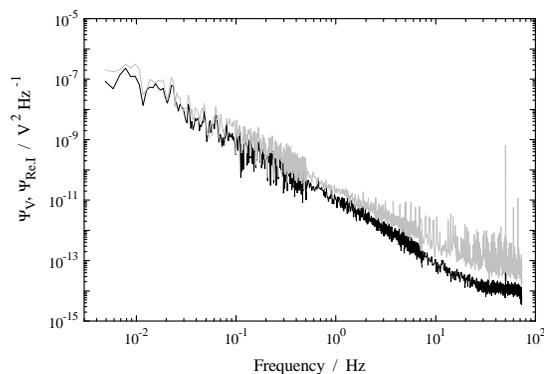

Figure 2. Power spectral densities of potential, $\Psi_V(f)$ (gray) and of the ohmic-drop fluctuations, $\Psi_{Re,I}(f)$ (black) induced by the *oer* on $PbO_2+Co_3O_4$ electrodes at 10 mA cm^{-2}.

References

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