ELECTRODE REACTIONS ON PLATINIZED EBONEX® POWDER IN HALOGENIDE SOLUTIONS

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Platinum was dispersed on the surface of Ebonex® (Ti_4O_7) powder by thermal decomposition of H_2PtCl_6. Catalytic activity of this composite catalyst was tested in the iodide and bromide oxidation reactions in water solutions using rotating disc electrode.

Materials

Titanium oxide Ti_nO_{2n-1} with *n* amounting predominantly to 4, (Magneli phase) is a commercial product (trademark name Ebonex®) characteristic of high chemical stability and a remarkable electronic conductivity, and therefore it is suitable to be used as a supporting material for the electrocatalyst for anodic processes. Ebonex powder was already investigated as a catalyst carrier for oxygen evolution in a fuel cell[1]. The particles of commercial product >10 μm in diameter, were platinized by thermal decomposition of H_2PtCl_6 dissolved in isopropyl alcohol. The Pt/Ebonex® mass ratio reached was 0.15. The function of supporting material is primarily to suppress the agglomeration of catalyst particles, however also one may expect the influence of catalyst/support interactions on catalyst effectiveness. The powdery material was applied on glassy carbon rotating disc using 5 % (by weight) of poly(vinylidene fluoride) as a binder. Since the catalyzed, polymer bonded powder alone displayed insufficient conductivity, an addition of 5% carbon black was necessary. In principle, for this investigation, one might use also a market available, compact, sintered piece of Ebonex®, which is always porous to some extent, however in that case it would be difficult to control the effective catalyst/Ebonex® mass ratio.

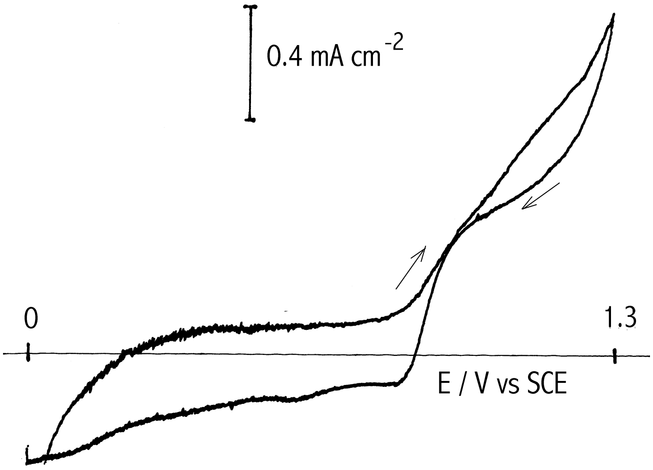

Fig. 1. *Voltammogram of bromide oxidation from 0.01 M NaBr in 1 M $HClO_4$ water solution, on rotating glassy carbon disc covered by a thin layer of platinized Ebonex® + 5% carbon black; both direct and reverse scans were recorded at a polarization rate 20 mV s^{-1} and rotation frequency 10 cps.*

Results

Fig 1. shows the voltammograms of bromide oxidation. On smooth platinum, this reaction starts at 0.8 V vs. SCE and displays a clearly expressed diffusion plateau. On platinized Ebonex® powder the current does not display diffusion limitation, however, the oxidation current is similar in intensity to that on smooth platinum in the region of diffusion limitations. The gain in this case consists however in the small amount of platinum used. Without carbon black addition, the oxidation proceeds at much slower rate. This indicates that poor electric contact between the Ebonex® particles and the glassy carbon support plays a considerable role in catalyst utilization degree. The electrode material, due to the developed surface, possess a high apparent double layer capacity, and therefore low polarization rate, 2 mV s^{-1} in this case, is required to suppress high background capacitance current, causing a high current difference when recorded in direct and opposite polarization directions..

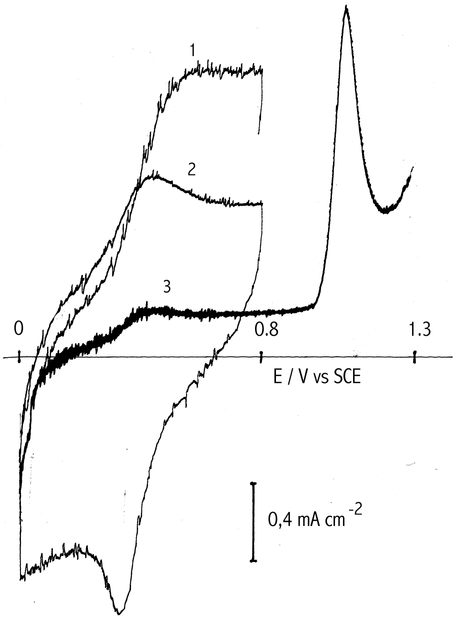

Fig. 2. *Voltammograms of iodide oxidation from 0.01 M KI in 1 M $HClO_4$ water solution, on rotating glassy carbon disc covered by a thin layer of platinized Ebonex® + 5% carbon black. Curve 1: scan rate 20 mV s^{-1}, rotation rate 10 cps; curve 2: stationary electrode, scan rate 20 mV s^{-1}; curve 3: stationary electrode, scan rate 2 mV s^{-1}*

In Fig. 2, iodide oxidation on platinized Ebonex® powder is demonstrated. The oxidation to tri-iodide ion starts at 0.35 V vs SCE, and reaches diffusion limitation, which may be proved by changing the rotation rate (see the curves 2 and 3). The decrease in the polarization rate reduces the background current, and just the curve 3, recorded at a polarization rate of 2 mV s^{-1}, may be considered as representing nearly stationary faradaic current. By enlarging final anodic potential, one can observe iodine oxidation to iodide, starting at nearly 1 V vs. SCE. All the processes of iodide oxidation are quite analogous to these observed on smooth platinum electrode in the same solution.

This work demonstrates that platinized Ebonex® powder may be successively applied as a catalyst for halogenide oxidations in water solutions.

References:

1. A.Hamnett, P.S.Stevens, R.D.Wingate, J.Appl.Electrochem., 21 (1991) 982

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