



HAL
open science

Formation and physicochemical properties of composite PbO₂ materials

Alexander B. Velichenko, T.V. Luk'Yanenko¹, Felix I. Danilov, Rossano
Amadelli, Didier Devilliers

► **To cite this version:**

Alexander B. Velichenko, T.V. Luk'Yanenko¹, Felix I. Danilov, Rossano Amadelli, Didier Devilliers.
Formation and physicochemical properties of composite PbO₂ materials. 6th International Conference
on Lead-Acid Batteries LABAT'2005, Jun 2005, Varna, Bulgaria. pp.200. hal-00163655

HAL Id: hal-00163655

<https://hal.science/hal-00163655>

Submitted on 17 Jul 2007

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

FORMATION AND PHYSICOCHEMICAL PROPERTIES OF COMPOSITE PbO₂ MATERIALS

A.B. Velichenko¹, T.V. Luk'yanenko¹, F.I. Danilov¹, R. Amadelli², D. Devilliers³

¹Ukrainian State University of Chemical Technology, Gagarin ave. 8, Dnepropetrovsk, 49005,

Ukraine velichenko@ukr.net

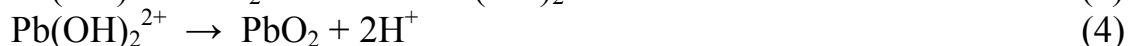
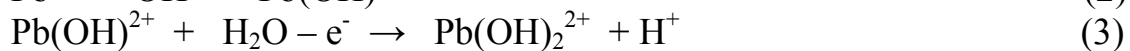
²ISOF-CNR and Dipartimento di Chimica, Universita' di Ferrara, via Borsari 46

- 44100 Ferrara - Italy

³Université Pierre et Marie Curie, 75252 PARIS Cedex 05 - FRANCE

There is a great interest in the improvement of lead dioxide based materials for use in different applications. Some metal ions present in the Pb(II) deposition solution are well incorporated into the PbO₂ matrix during electrodeposition (for example Bi³⁺, Fe³⁺, F⁻) to produce a doped oxide with improved reactivity and stability in comparison with pure PbO₂ [1-3]. In comparison, there is much less information on effects of polyelectrolytes and surfactants additives on the process of oxide electrodeposition and the physicochemical properties of the resulting materials [4-6]. In the present work we used some polyelectrolytes (Nafion[®], Drimax 1235, Magnafloc, gelatin, polyamino guanidinehydrochloride) and surfactants (potassium salt of nonafluoro-1-butanesulfonic acid, sodium dodecylsulphate, sodium lauretsulphate) as electrolyte additives for electrosynthesis of composite materials oxide-polyelectrolyte and oxide-surfactant.

It is shown that both polyelectrolytes and anionic surfactants are adsorbed on PbO₂. Despite additives adsorption on the oxide surface the mechanism of lead dioxide electrodeposition does not depend on the nature of polyelectrolyte or surfactant and it can be described by following scheme:



The first stage is the formation of oxygen-containing particles as OH_{ads}, chemisorbed on the electrode. In a subsequent chemical stage, these particles interact with lead species forming a soluble intermediate product, Pb(OH)²⁺ which is further oxidized electrochemically with transfer of the second electron forming a soluble oxygenated Pb(IV) compound. The latter is decomposed chemically to form colloidal PbO₂ particles in the electrolyte volume that then crystallize on the surface. At low overpotential the rate-determining stage is the second electron transfer reaction and at high overpotential the process is controlled by Pb²⁺ diffusion.

Some surfactants and polyelectrolytes, especially anionic ones, can adsorb on the positively charged PbO₂ particles (Fig. 1). At low overpotentials the influence of adsorption on the electron-transfer stage can be described by following equation [7-9]:

$$\frac{i_\theta}{i_{\theta=0}} = (1 - \theta) \exp(-S\theta) \exp\left[-\frac{(z + \beta n)F\Delta\psi'(\theta)}{RT}\right] \quad (5)$$

Polyelectrolytes inhibit lead dioxide electrodeposition mainly due to their adsorption on the PbO₂ coating that blocks some active centers on the electrode surface where further reaction takes place. Rarely anionic polyelectrolytes can accelerate the deposition process. For instance, the dependence of the constant rate for PbO₂ electrodeposition on the concentration of Nafion[®] added to the deposition solution has a volcano shape (Fig. 1). At low content of Nafion[®] in the solution the constant rate of the process increases with increasing the additive concentration, probably due to ψ'

effect. At higher Nafion[®] contents in the solution, the process is inhibited due to the site blocking effect.

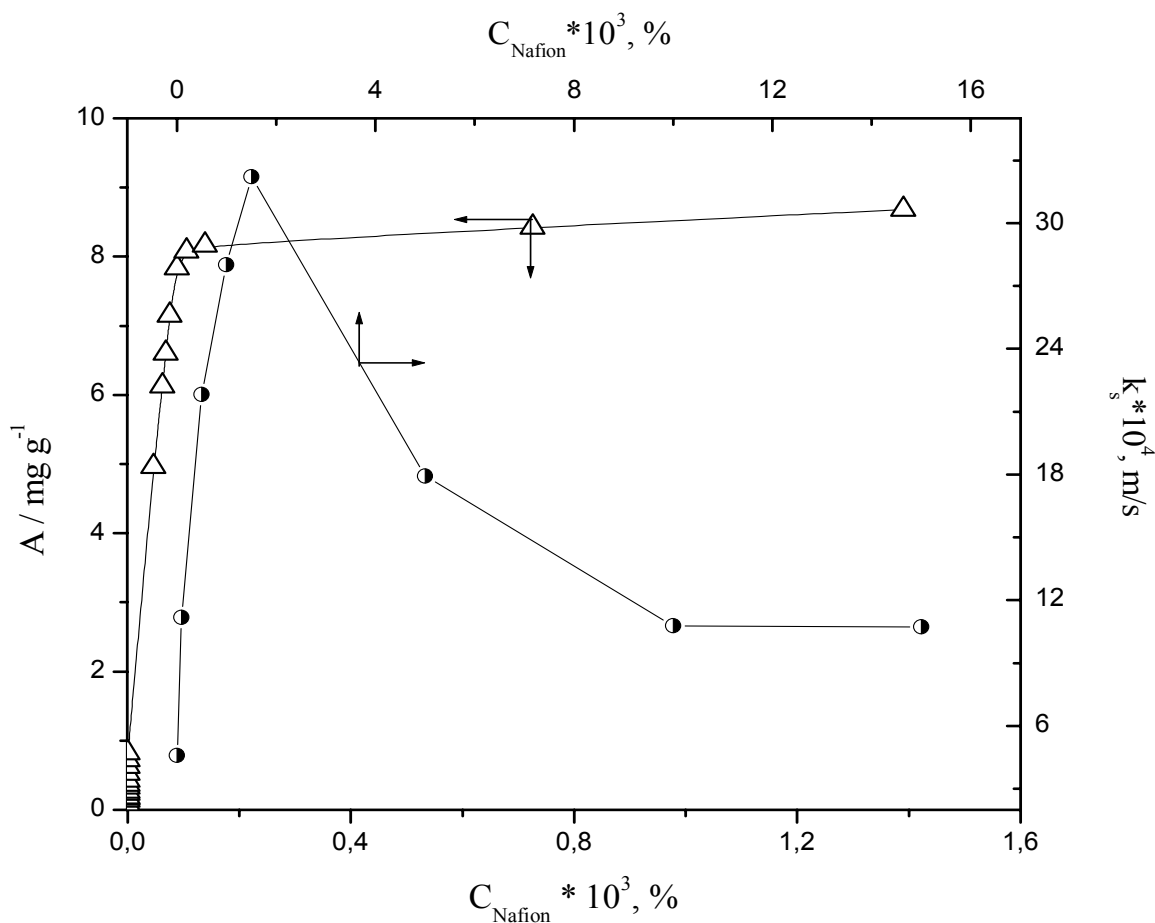


Fig. 1. Effect of the content of Nafion[®] polymeric additive in the electrolyte (0.1M HNO₃ + 0.1M Pb(NO₃)₂) on the constant rate of the second electron transfer stage (3). Adsorption isotherm on PbO₂ powder.

It was shown that the nature of additives strongly influences on the PbO₂ formation rate on Pb anode in sulfuric acid. Some additives, for instance F⁻, accelerate formation of PbO₂ and other ones (ions of iron group, surfactants and polyelectrolytes) inhibit oxide formation on the lead anode.

Table 1. Effect of nitric acid concentration on the Nafion[®] content in the composite material ($i = 4 \text{ mA/cm}^2$).

N ^o	Electrolyte composition	Nafion [®] in PbO ₂ , wt. %
1	0.1 M HNO ₃ + 0.1 M Pb(NO ₃) ₂ + 0.05 % wt. Nafion [®]	7.0
2	0.5 M HNO ₃ + 0.1 M Pb(NO ₃) ₂ + 0.05 % wt. Nafion [®]	8.7
3	1.0 M HNO ₃ + 0.1 M Pb(NO ₃) ₂ + 0.05 % wt. Nafion [®]	10.2
4	2.0 M HNO ₃ + 0.1 M Pb(NO ₃) ₂ + 0.05 % wt. Nafion [®]	13.1
5	3.0 M HNO ₃ + 0.1 M Pb(NO ₃) ₂ + 0.05 % wt. Nafion [®]	17.0

It is interesting to note that both polyelectrolytes and surfactants are incorporated into the deposited lead dioxide forming a composite material. The additive content in the lead dioxide can change from 1 wt. % to 20 wt. % depending from the electrodeposition conditions and the

electrolyte composition (Fig. 2, Table 1). The colloidal-electrochemical mechanism of the composite formation was proposed, which include electrochemical formation of oxide particles in the solutions volume (6), adsorption of polyelectrolyte and surfactants on the oxide particles (7), their electrophoresis to the electrode (for particles with negative ξ -potential) with further crystallization on the anode surface (8):

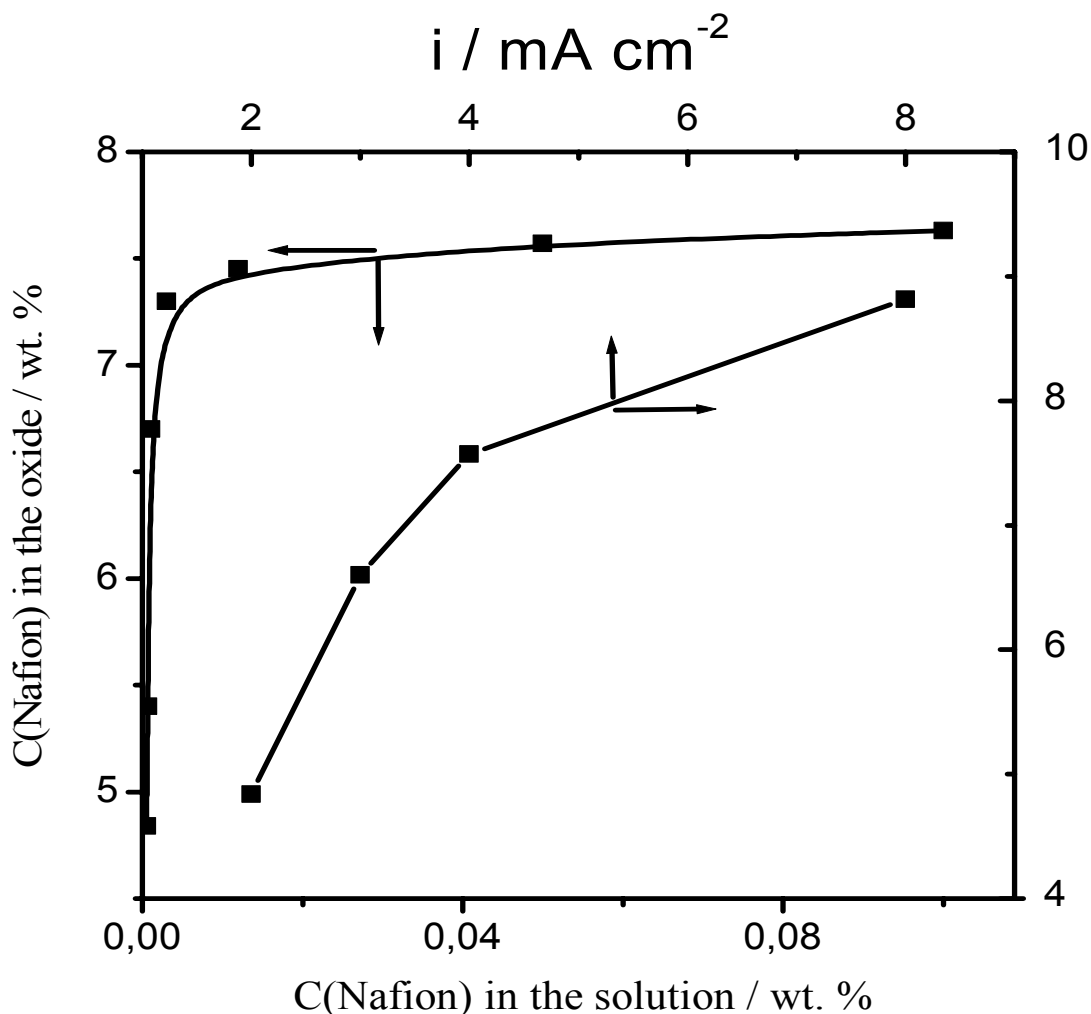
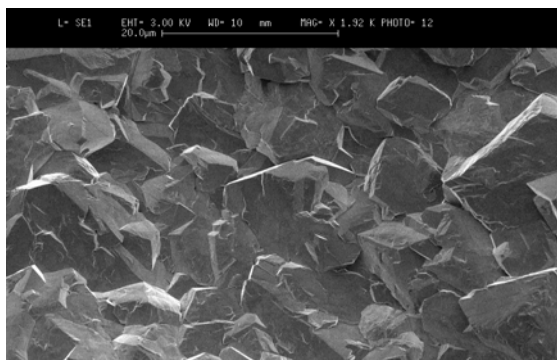


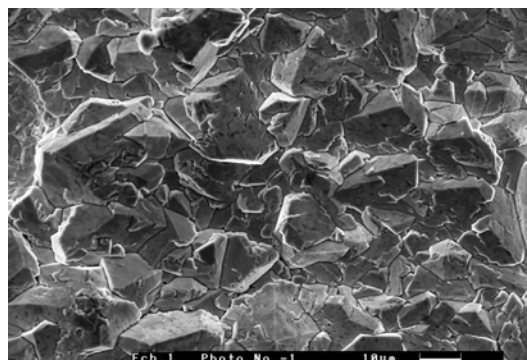
Fig. 2. Effect deposition current density (i) and concentration polymeric additive (C_{Nafion}) on the Nafion[®] content in the composite material.

It is important to note that in the presence of polyelectrolytes and surfactants submicro- and nano-crystalline coatings are formed (Fig. 3). In most cases the PbO_2 films were a mixture of the α - and β -phases, the latter being prevalent. An examination of the XRD spectra shows that peak intensities generally decrease with increasing surfactants and polyelectrolytes content in the composite. This indicates that the grain size is smaller for the lead dioxide films in the composite materials. Difference in intensity provides sufficient evidence of the existence of an amorphous phase and it is a good agreement with SEM data.

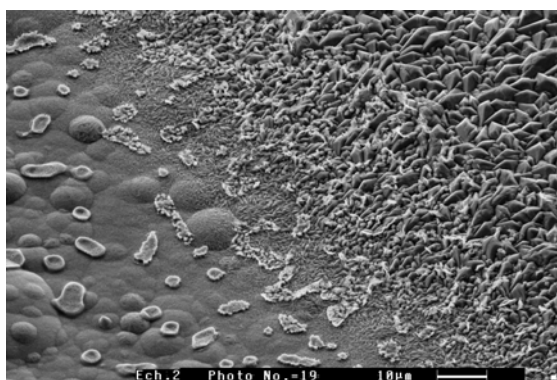
It was shown that physicochemical properties of the materials and their electrochemical behaviour strongly depend from nature and content of additive in the composites.



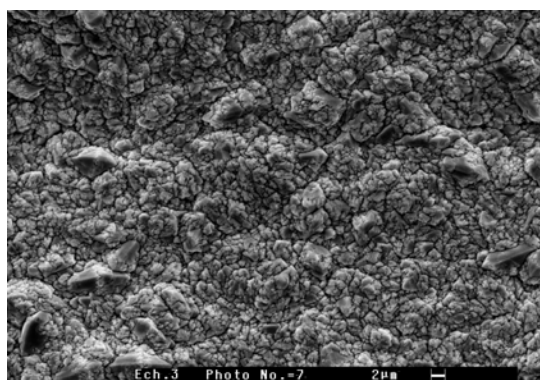
a



b



c



d

Fig 3. SEM images of lead dioxide (a) and composite material oxide-polymer with different content of Nafion[®] (wt. %): b – 3.5; c – 7.0; d – 17.0 %.

References

1. I.-H.Yeo, Y.S. Lee, D.C. Johnson, *Electrochim. Acta.* 37 (1992) 1811.
2. S. Cattarin, I. Frateur, P. Guerriero, M. Musiani, *Electrochim. Acta.* 46 (2001) 4229.
3. A.B.Velichenko, R. Amadelli, G.L. Zucchini D.V. Girenko, F.I. Danilov, *Electrochim. Acta*, 45 (2000) 4341.
4. A.B. Velichenko, T.V. Luk'yanenko, R. Amadelli, F.I. Danilov, *Ukr. Chem. J.* 70 (2004) 45.
5. Wen Ten-Chin, Wei Ming-Gwo, Lin Kwang-Lung, *J. Electrochem. Soc.* 137 (1990) 2700.
6. P.R. Ramachandran, V. Nandakumar, K.V. Venkateswaran, *Trans. Indian Inst. Met.* 49 (1996) 789.
7. A.N. Frumkin, *Doklady AN SSSR* 85 (1952) 373.
8. Damaskin B.B. *Electrode processes in solutions of organic compounds*, MSU, Moscow, 1985.
9. M.A. Loshkaryov, F.I. Danilov, G.E. Bol, L.G. Sechin, *Electrokhimiya* 13 (1977) 593.