



PHYSICAL CHEMISTRY 2016

*13th International Conference on
Fundamental and Applied Aspects of
Physical Chemistry*

*Proceedings
Volume I*

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Organized by

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Serbia*

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FORMATION OF HYDROQUINONE AND CATECHOL DURING ELECTROOXIDATION OF PHENOL ON CLAY-MODIFIED ELECTRODES

T. Mudrinić, A. Ivanović-Šašić, M. Ajduković, Z. Mojović and D. Jovanović

University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, 11000 Belgrade, Serbia. (tihana@nanosys.ihm.bg.ac.rs)

ABSTRACT

Clay was modified by pillaring, which was performed by combinations of pillaring cations: Al^{3+} and Fe^{3+} or Al^{3+} , Fe^{3+} and Ni^{2+} . The synthesized materials were used to obtain glassy carbon electrode (GCE) coatings. Electrochemical oxidation of phenol from acidic solution was investigated on clay-modified electrodes by method of cyclic voltammetry. As a consequence of electrode fouling the peak current registered in the tenth cycle dropped in the comparison to the current obtained in the first cycle. The first-order derivative linear sweep voltammetry was used in the analytical procedure. Hydroquinone/catechol current ratio increased in the opposite manner to the phenol oxidation current drop.

INTRODUCTION

Electrooxidation of phenol has been studied as a model reaction as well as due to phenols classification as a priority contaminant [1]. Oxidation mechanism of phenol is well-known [2]. Electrooxidation mechanism starts with the formation of phenoxy radical. Phenoxy radicals can be further oxidized to oxidation products like hydroquinone, quinone etc, or can be involve in polymerization reaction. Polymerization reaction leads to formation of insulating film on the electrode surface and passivates electrode. Literature results showed that electrodes, such as graphite, IrO_2 , RuO_2 and Pt rapidly passivate. Complete phenol oxidation to CO_2 is favored on antimony-doped tin oxide, lead or boron-doped diamond electrodes. Unfortunately, these electrodes encounter several problems such as short service life, the release of toxic ions and high cost, respectively [3]. Modification of the electrode surface can improve electrode performances. Clay minerals have been extensively studied as electrode surface modifiers due to their availability, well-defined layered structure, thermal and chemical stability and low cost [4]. Therefore, either clay modifications or designed clay synthesis are used for the preparation of clay-modified

electrodes. Pillaring is one of the common techniques of clay modification. It was shown that the electrocatalytic activity and stability depend on the type of incorporated metals. Electrode modified with clay pillared with Al, Fe, Ni polyhydroxy cations showed the best stability, regarding electrode fouling due to polymer formation [5], in comparison to electrode modified with clay pillared with other transition metals (Al,Fe; Al,Co and Al,Cu) [6]. The goal of this work was to investigate the influence of hydroquinone and catechol formation on clay-modified electrode with the degree of its passivation during electrooxidation of phenol. In order to investigate the effect, a series of modified bentonite based materials was synthesized. Clay from seldom investigated deposit Mečji Do in Serbia was modified by pillaring, which was performed using the following combinations of pillaring cations: Al^{3+} and Fe^{3+} or Al^{3+} , Fe^{3+} and Ni^{2+} . The synthesized materials were used to obtain glassy carbon electrode (GCE) coatings.

EXPERIMENTAL

Bentonite clay from seldom investigated deposit Mečji Do, Serbia was used as a raw material. The raw clay was subjected to the common Na-exchange procedure and denoted as Na-MD. The process of pillaring was carried out according to previously established procedure [6]. Pillaring solutions were adjusted to have the molar ratio of $\text{OH}^-/\text{Me}^{n+} = 2.0$ (where $\text{Me}^{n+} = \text{Al}^{3+}$, Fe^{3+} , Ni^{2+}) and metal cation/clay ratio of 10 mmol Me^{n+}/g . The pillaring solutions contained the following molar ratios of each species: a) 90% Al and 10% Fe and b) 90% Al, 5% Fe and 5% Ni. Accordingly, the obtained pillared samples were denoted: AlFe10-MD and AlFe5Ni5-MD, respectively. The drop of dispersion of investigated sample with 10 wt. % of carbon black in 5 wt. % Nafion was applied on the surface of glassy carbon electrode. The electrochemical response of samples was tested by method of cyclic voltammetry at polarization rate 10 mVs^{-1} in the range of potential from hydrogen evolution at -0.3 V to oxygen evolution at 1.1 V . First, prepared electrodes were tested in $0.1 \text{ M H}_2\text{SO}_4$. Then, the freshly prepared electrodes were tested in $0.01 \text{ M phenol} + 0.10 \text{ M H}_2\text{SO}_4$. All potentials are reported versus Ag/AgCl (3 M KCl) reference electrode, and platinum rod served as counter electrode.

RESULTS AND DISCUSSION

Cyclic voltammograms (CVs) obtained in acid solution and phenol containing solution were similar for Na-MD and AlFe10-MD. For clarity sake CVs for AlFe10-MD and AlFe5Ni5-MD are presented in Figs. 1 and 2. The CV obtained in acid solution (dashed line in Figs. 1a and 2a) is presented together with the first cycle obtained in phenol containing solution

(solid line in Fig. 1a and 2a). CVs obtained in acid solution showed a pair of peaks around 0.45 V attributed to oxidation/reduction of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple [5]. In the first cycle of the electrooxidation of phenol, phenol oxidation wave and two cathodic peaks were obtained on all investigated electrodes (Fig. 1a and 2a). From the second to tenth cycle two additional anodic peaks appeared (Fig. 1b and 2b).

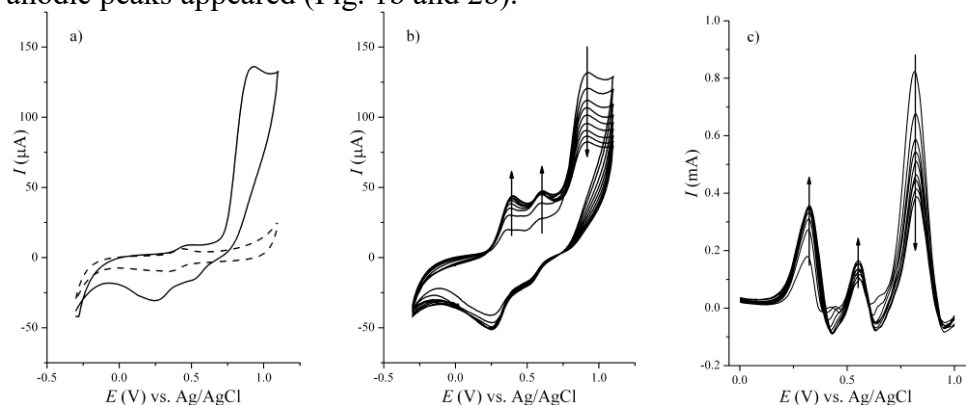


Figure 1. Cyclic voltammograms of AlFe10-MD electrode: (a) in 0.1 M H_2SO_4 (dashed line) and the first scan in 0.01 M phenol+0.1 M H_2SO_4 (solid line) (b) successive cycles in 0.01 M phenol+0.1 M H_2SO_4 and (c) The first-order derivative linear sweep voltammograms.

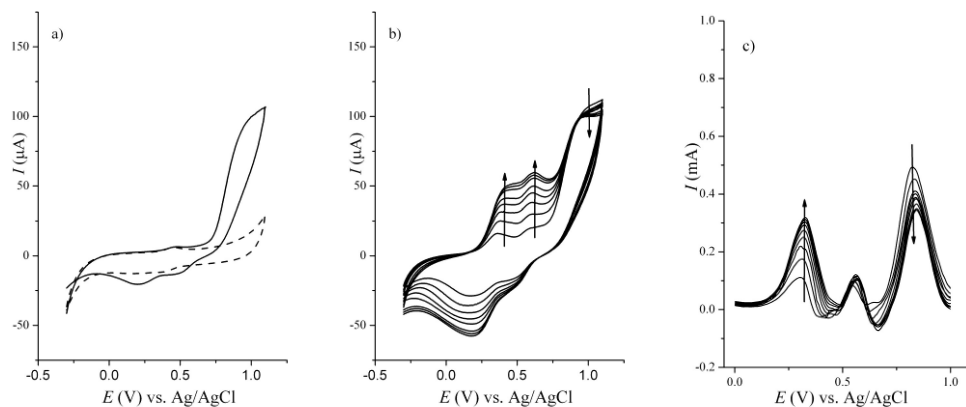


Figure 2. Cyclic voltammograms of AlFe5Ni5-MD electrode: (a) in 0.1 M H_2SO_4 (dashed line) and the first scan in 0.01 M phenol+0.1 M H_2SO_4 (solid line) (b) successive cycles in 0.01 M phenol+0.1 M H_2SO_4 and (c) The first-order derivative linear sweep voltammograms.

The obtained cathodic and anodic pairs of peaks corresponded to the oxidation/reduction of hydroquinone and catechol. After 10 cycles, the current of the phenol oxidation peak on the Na-MD and AlFe10-MD electrodes decreased substantially (52.1 % and 41.2 %, respectively) as a

consequence of electrode fouling. In the case of Ni containing electrode the stability was significantly improved. The AlFe5Ni5-MD based electrode showed phenol oxidation current decrease of 5.4 % during ten CV cycles. In order of sensitivity of detection to be improved, the first-order derivative linear sweep voltammetry was used in the analytical procedure (Fig. 1c and 2c). The hydroquinone/catechol current ratio was 1.3, 2.2 and 3.1 for Na-MD, AlFe10-MD and AlFe5Ni5-MD, respectively. According to Li et al. [2] polymerization can also proceed via phenoxy radicals attack either on hydroquinone or catechol. According to the findings presented in this work it can be concluded that catechol is more likely candidate for polymerization reaction than hydroquinone. Addition of nickel ion in the structure of modified clay probably promoted hydroquinone formation path over catechol formation path.

CONCLUSIONS

Pillared clays were used as modified electrodes for the electrooxidation of phenol. Clays were pillared by combination of cations: Al^{3+} and Fe^{3+} or Al^{3+} , Fe^{3+} and Ni^{2+} . Cyclic voltammograms recorded from 0.01 M phenol + 0.10 M H_2SO_4 showed phenol oxidation current decrease of 52.1%, 42.1% and 5.4% for Na-MD, AlFe10-MD and AlFe5Ni5-MD based electrode, respectively. The first-order derivative linear sweep voltammetry was used in the analytical procedure. Hydroquinone/catechol current ratios were 1.3, 2.2 and 3.1 for Na-MD, AlFe10-MD and AlFe5Ni5-MD, respectively.

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REFERENCES

- [1] Environmental Protection Agency, Appendix A to Part 423—126 Priority Pollutants, (2014)
- [2] X. Li, Y. Cui, Y. Feng, Z. Xie, J. Gu, *Water Research*, 2005, **39**, 1972-1981.
- [3] M. Panizza in: *Electrochemistry for the Environment*, C. Comninellis, G. Chan (Eds.), Springer, New York, 2010.
- [4] L. Fernández, C. Borrás, H. Carrero, *Electrochimica Acta*, 2006, **52**, 872-884.
- [5] T. Mudrinić, Z. Mojović, A. Milutinović-Nikolić, P. Banković, B. Dojčinović, N. Vukelić, D. Jovanović, *Electrochimica Acta*, 2014, **144**, 92-99.
- [6] P. Banković, Z. Mojović, A. Milutinović-Nikolić, N. Jović-Jovičić, S. Marinović, D. Jovanović, *Applied Clay Science*, 2010, **49**, 84 -89.