



**PHYSICAL CHEMISTRY 2012**

<sup>11</sup>th International Conference  
on Fundamental and Applied Aspects of  
Physical Chemistry

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Under the auspices of the  
University of Belgrade

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Proceedings

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The Conference is dedicated to  
Professor Ivan Draganić

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## ORGANIZERS

PHYSICAL CHEMISTRY 2012

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Fundamental and Applied Aspects of  
Physical Chemistry*

*Under the auspices of the  
University of Belgrade*

*Organized by  
The Society of Physical Chemists of  
Serbia*

*in co-operation  
with*

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*Boriskov Institute of Catalysis of Siberian Branch of the Russian Academy  
of Sciences*

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D-07-P

## **DYNAMIC INSTABILITY OF METHANOL OXIDATION FROM ALKALINE SOLUTION ON STATIONARY PT ELECTRODE**

T. Mudrinić<sup>1\*</sup>, Z. Mojović<sup>1</sup>, A. Abu Rabi-Stanković<sup>1</sup>, N. Jović-Jovičić<sup>1</sup>,  
S. Marinović<sup>1</sup>, M. Milenković<sup>2</sup>, D. Stanisavljev<sup>2</sup>

<sup>1</sup>*IHTM-Center of Catalysis and Chemical Engineering, Njegoševa 12, Belgrade*  
<sup>2</sup>*Faculty of Physical Chemistry, Belgrade University, Studentski Trg 12, Belgrade,*  
*\*tihana@nanosys.ihtm.bg.ac.rs*

### **Abstract**

Cyclic voltammetry (CV) was used to study the dynamic instability of electrochemical oxidation of methanol in alkaline solution at stationary platinum electrode. Methanol oxidation was carried out in bicarbonate, carbonate and different pH values of sodium hydroxide solution. Experiments were conducted with and without previous stabilization of the working electrode in alkaline solution.

### **Introduction**

The occurrence of dynamic instabilities in electrochemical systems are a widespread phenomena such as periodic oscillations, quasiperiodic oscillations, chaos and mixed-mode oscillations [1]. Many investigations on complex electrochemical instabilities were conducted under conditions where either the current or the potential of the working electrode was held constant. Schell et al. [2-3] have investigated the occurrence of instability using cyclic voltammetry. The CVs revealed high-order periodic as well as aperiodic behavior that appeared during electro-oxidation of methanol in alkaline solution using rotating platinum electrode. The various types of CV behavior were found by systematically varying different control parameters: upper potential limit (UPL), lower potential limit (LPL), concentration of methanol, rotation rate and sweep rate.

In this paper, cyclic voltammetry was used to study the dynamic instability during methanol oxidation in alkaline solution on stationary Pt electrode at different UPL values. Electro-oxidation of methanol was carried out in bicarbonate, carbonate and different pH values of sodium hydroxide solution.

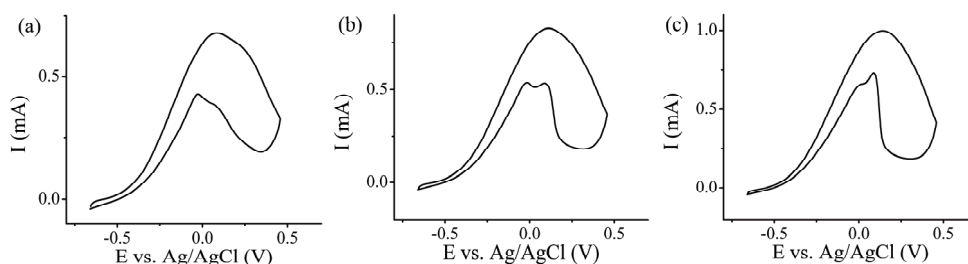
### **Experimental**

Electro-oxidation of methanol was investigated in 0.01 M, 0.1 M, 0.5 M, 1 M NaOH, 0.01 M NaHCO<sub>3</sub> and 0.01 M Na<sub>2</sub>CO<sub>3</sub> solutions that contained 1M CH<sub>3</sub>OH. Platinum electrode was pretreated in alkaline solution by cycling in the potential range from -600 mV to +600 mV until stable CV was obtained. The electrode was then transferred to the alkaline solution containing methanol. The cycling was performed from same LPL while UPL was varied in the range from 300 to 580 mV. For each UPL value 50 cycles were performed. Methanol electro-oxidation

was also investigated on fresh Pt electrode without previous pretreatment in the alkaline solution. All measurements were recorded at polarization rate of 100 mV/s. The device used for electrochemical measurements was Gamry PCI4G750-51093. The reference electrode was Ag/AgCl, KCl (3M), while a platinum foil served as a counter electrode. Working electrode was rectangular shaped (10 × 3 mm) platinum electrode.

## Results and discussion

Three CVs shown in Fig.1 provide representations of the general phenomena considered in this paper. These CVs were recorded during cycling of stationary Pt electrode in 1M CH<sub>3</sub>OH + 0.01 M NaOH with UPL set at +460 mV. The working electrode was previously stabilized in 0.01 M NaOH. During the forward sweep one peak appeared at potential of 0.0 V vs. Ag/AgCl. At the reverse scan, two peaks were visible. The relative intensity of these peaks was alternately changing with number of cycle.



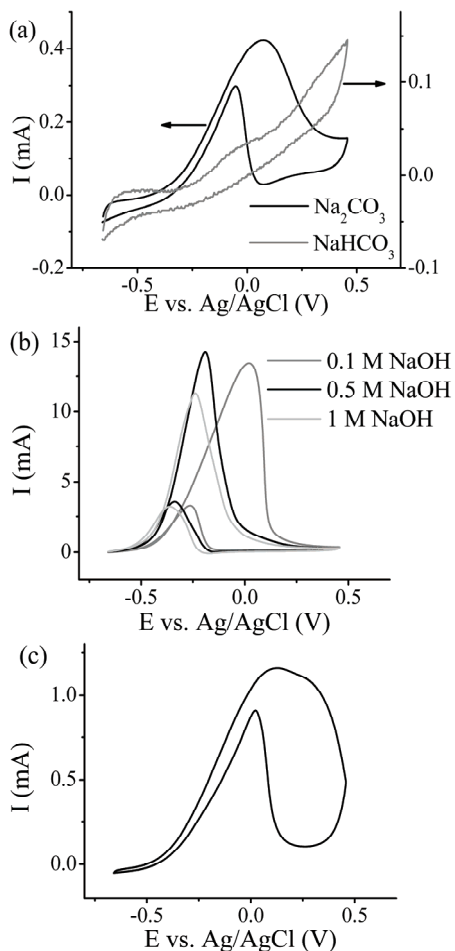
**Figure 1** The CVs of stationary Pt electrode in 1M CH<sub>3</sub>OH + 0.01 M NaOH, recorded at polarization rate of 100 mV/s with UPL set at +460 mV. Pt electrode was previously stabilized in 0.01 M NaOH. (a) 21<sup>th</sup> cycle (b) 29<sup>th</sup> cycle and (c) 37<sup>th</sup> cycle.

The CVs of electro-oxidation of methanol in different alkaline solutions and pH values of sodium hydroxide solution, obtained at same conditions as in Fig. 1, are presented in Fig. 2a and 2b, respectively. CV obtained in the 1M CH<sub>3</sub>OH + 0.01 M NaOH during the experiment performed without previous stabilization of working electrode is shown in Fig. 2c. The phenomenon, shown in Fig. 1, was not observed under all other investigated conditions.

Tripković et al. [4-5] studied methanol oxidation on platinum surface in alkaline media (NaOH, Na<sub>2</sub>CO<sub>3</sub> and NaHCO<sub>3</sub>) and they found that surface activity was correlated with OH<sub>ad</sub> coverage on Pt. Investigation has shown that bicarbonate and carbonate anions influence the OH<sup>-</sup> ion adsorption, as well as the methanol oxidation itself. In fact, these anions decrease the surface activity in the oxidation of methanol by blocking the sites available for OH<sup>-</sup> ion or methanol adsorption. The surface activity decreases in the sequence sodium hydroxide > carbonate > bicarbonate solution. Therefore, it can be assumed that adsorption of HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> ions from carbonate and bicarbonate solutions on surface of Pt were responsible for absence of phenomenon shown in Fig. 1. The absence of instable electrochemical behavior in solutions with different pH values, Fig. 2b was



probably influenced by OH adsorption. In order to obtain phenomenon of dynamic instability, of electro-oxidation of methanol the working stationary Pt electrode must be previously stabilized in alkaline solution and also the proper ratio of NaOH and CH<sub>3</sub>OH concentrations in solution must be provided.



**Figure 2** The CVs of stationary Pt electrode in (a) different alkaline solution (b) different pH values of sodium hydroxide solution (c) 1M CH<sub>3</sub>OH + 0.01 M NaOH, without previous stabilization of the working electrode in alkaline solution. Other conditions are the same as in Fig. 1.

### Conclusions

In this paper the dynamic instability, during electro-oxidation of methanol from alkaline solution using stationary Pt electrode was studied by cyclic voltammetry. Methanol oxidation was carried out in bicarbonate, carbonate and different pH values of sodium hydroxide solution. The phenomenon of alternately changing relative intensity of two peaks obtained at the reverse scan with number of cycle was only found using the ratio of concentration of sodium hydroxide and methanol 1:100. The other important factor for appearance of this phenomenon was stabilization of working electrode in the alkaline solution.

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