

# Ethanol oxidation at metal–zeolite-modified electrodes in alkaline medium. Part 2: palladium–zeolite-modified graphite electrode

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**Abstract** Impregnated Pd–zeolite graphite (PdZG) electrodes have been tested for ethanol oxidation in 0.5 M NaOH. The results obtained have been compared with that of Pd electrode. Cyclic voltammetric and chronoamperometric measurements indicated the activity of PdZG electrode toward ethanol oxidation and poisoning tolerance. The influence of zeolite loading as well as impregnation time in Pd<sup>2+</sup> solution has been examined. Scan rate effect and ethanol concentration dependency indicated that ethanol oxidation at PdZG electrode was governed by diffusion control.

## Introduction

High surface area electrocatalytic electrode such as Pt, Pd, and Au are of interest for fuel cell technology. The high surface area electrocatalysts can be made by sintering, electrodeposition, or dispersion of active electrocatalytic materials on a support with a relatively high surface area [1–15]. Zeolite exhibits an advantage compared to other classical support materials. It has a large specific area with strongly organized microporous channel systems in which both a regular and high dispersion of metal nanoparticles can be obtained. Accordingly, recent research effort has been directed toward the use of Pt–zeolite-modified electrodes for alcohol oxidations [16–18] in order to obtain a higher catalytic activity while keeping the Pt content as low as possible. This is of great importance for fuel cell application and commercialization.

It is well known that palladium is not a good electrocatalyst for methanol oxidation, but it shows excellent higher activity and better steady-state electrolysis than Pt for ethanol electrooxidation in alkaline media [19, 20]. The use of Pd is of interest as it is at least 50 times more abundant on the earth than Pt. In addition to that, direct ethanol fuel cells have attracted more and more attention as ethanol is less toxic compared to methanol and can be considered as renewable fuel, as it can be easily produced in great quantity by the fermentation of sugar-containing raw materials and biomass [21]. The present work deals with modification of zeolite matrix with different amount of Pd and testing it for ethanol oxidation in alkaline medium. The performance of palladium–zeolite-modified graphite electrode in comparison with that of massive palladium toward the same reaction is the principal objective of the present investigations.

## Experimental

Electrolytic solutions were prepared from analytical grade chemicals NaOH (Merck) and C<sub>2</sub>H<sub>5</sub>OH (British Drug House) using distilled water produced by a Megapure system (MP-A6 Corning).

Zeolite suspension was made by dispersing a defined weight of NaY–zeolite (0.024, 0.048, 0.072, or 0.096 g) through ultrasonic vibration in 6-ml distilled water.

A Pt wire and Ag/AgCl electrode served as counter and reference electrodes, respectively. Cyclic voltammetric as well as chronoamperometric measurements were obtained using Metrohm 693 VA processor after modification of its 694 VA stand to adapt to our home-made solid electrode.

A graphite disc (Union Carbide) with geometric surface area of 0.294 cm<sup>2</sup> was used as a substrate for the modified

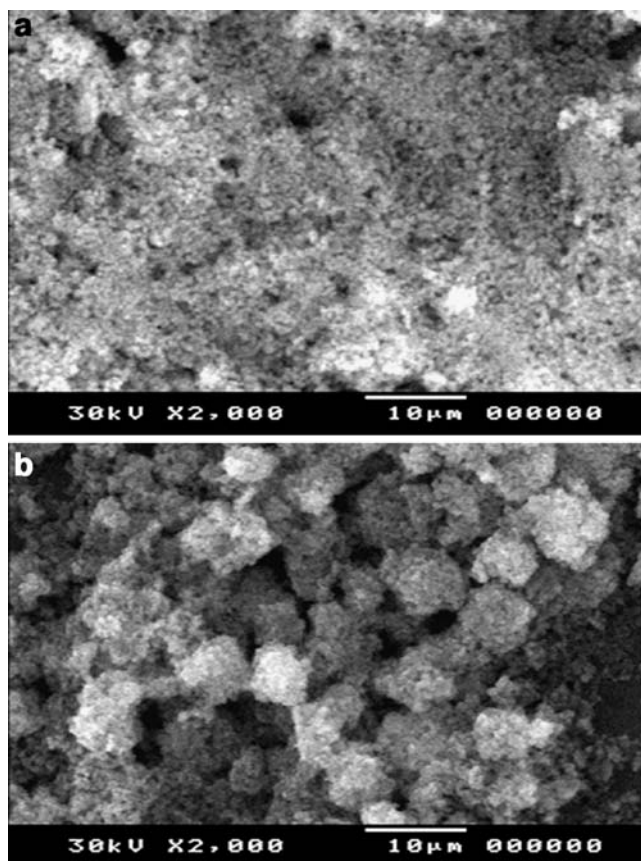
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working electrode. The graphite substrate was bonded to a Teflon tube [22] and subjected before modification to a polishing procedure as described elsewhere [23]. The electrode modification was accomplished by transferring one drop of aqueous zeolite suspension to the electrode surface, where it was allowed to dry.

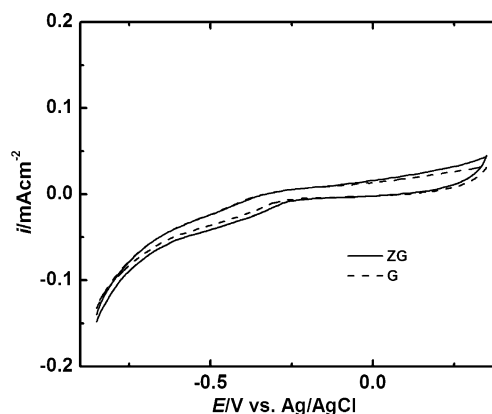
Finally, the electrode was immersed in  $10^{-5}$  M  $\text{PdCl}_2$  solution of pH=3 for different soaking times. The electrode was then inserted into the electrochemical cell containing 0.5 M NaOH and finally cycled between  $-0.85$  and  $0.35$  V versus Ag/AgCl until a steady-state voltammogram was obtained.

The Pd real surface area has been determined from the oxygen reduction peak [24].

Scanning electron microscopy (SEM) was performed (using SEM model JEOLSM 5410, Japan) in order to analyze the surface of the samples. Figure 1 shows the micrographs of NaY-zeolite-modified (Fig. 1a) and Pd-supported electrode (Fig. 1b). Figure 1a shows that the zeolite layer consists of homogenous crystals. After soaking the electrode in  $10^{-5}$  M  $\text{PdCl}_2$  solution (Fig. 1b), one can notice that a part of the electrode surface is doped with Pd particles.



**Fig. 1** a Scanning electron micrograph for the ZG electrode. b Scanning electron micrograph for the PdZG electrode obtained after soaking in  $\text{PdCl}_2$  solution for 8 min

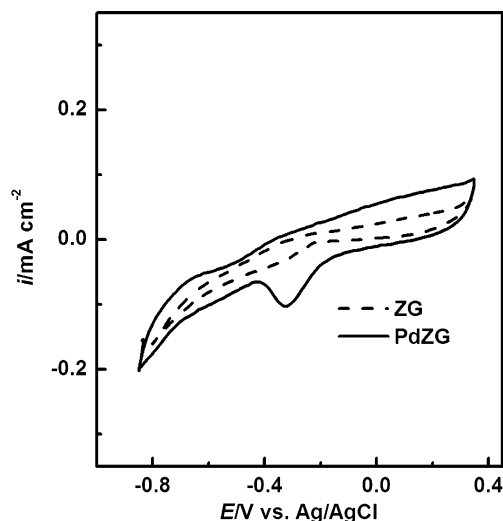


**Fig. 2** Cyclic voltammograms of (dashed line) G and (solid line) ZG electrodes in 0.5 M NaOH. Scan rate= $50 \text{ mV s}^{-1}$

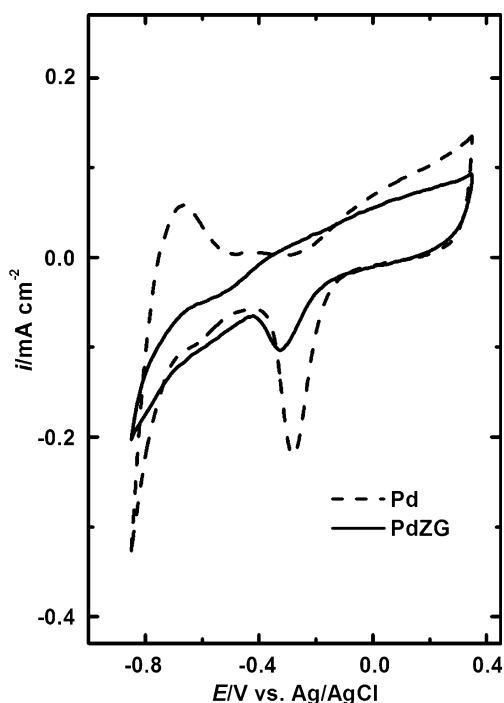
## Result and discussion

Figure 2 shows the cyclic voltammograms of graphite electrode in 0.5 M NaOH before and after modification with NaY-zeolite. The increase in the oxidation current above 0.2 V followed by increase in the reduction current below  $-0.35$  V is observed. This can be attributed to the oxidation–reduction process of oxygen species in zeolite. In addition, the additional resistance obtained from the presence of zeolite particles on the electrode surface cannot be excluded. These two reasons led to the inclination of the baseline of the voltammogram [25].

Figure 3 shows the voltammograms recorded for zeolite-modified graphite electrode (ZG) before and after soaking in  $10^{-5}$  M  $\text{PdCl}_2$  solution for 35 min. A remarkable difference especially in the potential range of palladium oxide formation/reduction region can be observed. The inclination of the base line [25] for the voltammogram of PdZG electrode can be attributed, as in the case of AuZG



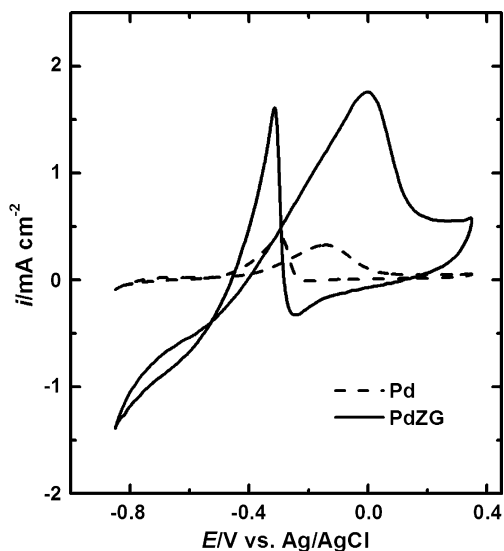
**Fig. 3** Cyclic voltammograms of ZG (dashed line) and PdZG (solid line) (soaking time=35 min) electrodes in 0.5 M NaOH.  $v=50 \text{ mV s}^{-1}$



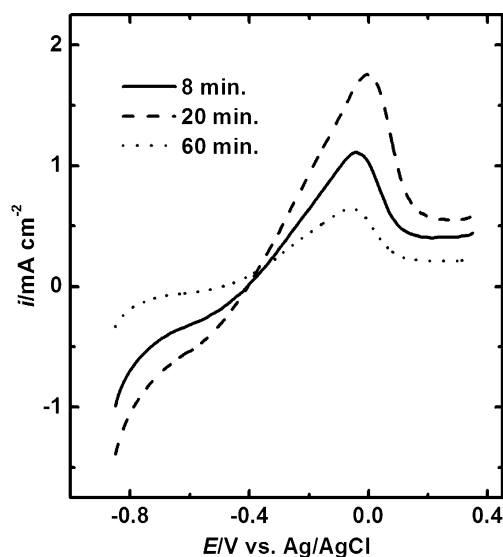
**Fig. 4** Cyclic voltammograms of Pd (dashed line) and PdZG (solid line) (soaking time=35 min.) electrodes in 0.5 M NaOH.  $v=50 \text{ mV s}^{-1}$

electrode [22], to the additional resistance obtained from the presence of zeolite particles and the oxidation–reduction process of oxygen species in zeolite layer [25]. This inclination in baseline has been reported previously for all electrodes modified with aluminosilicate materials [26–28]

Figure 4 shows a comparison between the voltammograms of massive Pd and PdZG electrodes recorded in sodium hydroxide solution. Careful examination of this



**Fig. 5** Cyclic voltammograms of Pd (dashed line) and PdZG (solid line) (soaking time=20 min.) electrodes in 0.5 M C<sub>2</sub>H<sub>5</sub>OH+0.5 M NaOH.  $v=50 \text{ mV s}^{-1}$



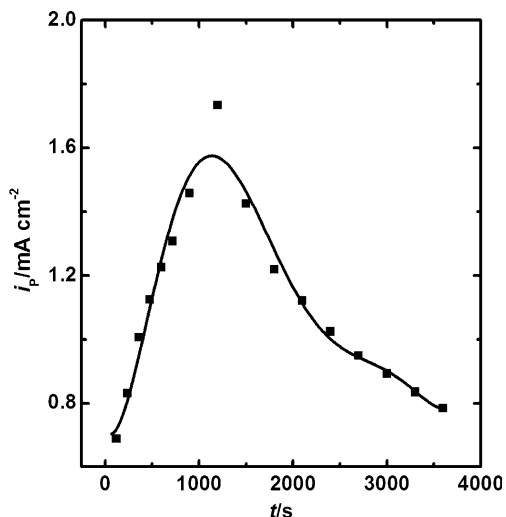
**Fig. 6** Anodic sweep of PdZG electrode in 0.5 M C<sub>2</sub>H<sub>5</sub>OH+0.5 M NaOH after soaking in PdCl<sub>2</sub> solution for 8 min (solid line), 20 min (dashed line), and 60 min (dotted line),  $v=50 \text{ mV s}^{-1}$

figure indicates that the onset of Pd oxide formation in case of PdZG electrode has been shifted into negative direction. Accordingly, sweeping the potential to the same upper limit for both electrodes leads to formation of strong palladium oxide layer in case of PdZG electrode. This is confirmed by the shift observed for the oxide reduction peak during the reverse scan to more negative potential value in case of PdZG compared to Pd electrode. In addition to that, high negative current was observed in the hydrogen adsorption/desorption region (this is also observed in the presence of ethanol but decreases as ethanol concentration increases). This may be connected to the activity of nano-Pd particles trapped in the zeolite matrix toward some reduction process, probably hydrogen.

The voltammograms recorded for PdZG electrode in 0.5 M NaOH+0.5 M ethanol are shown in Fig. 5. For the sake of comparison, the voltammogram recorded for massive Pd electrode under the same experimental condition is also included. The main differences observed are:

1. The onset of ethanol oxidation starts at more negative potential in case of PdZG, leading to a broader oxidation peak during the positive sweep than on massive palladium.
2. The peak current density is higher in case of PdZG electrode.

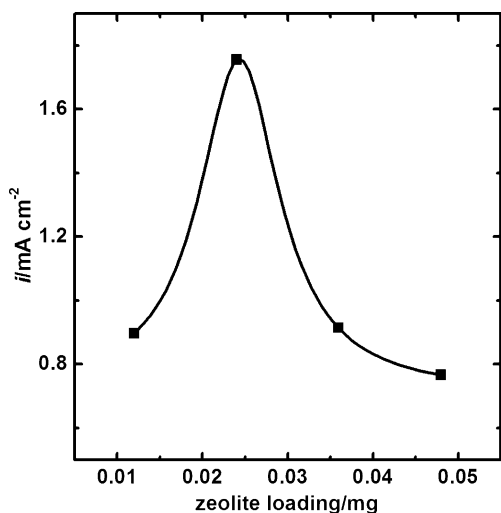
This may be taken as evidence that PdZG electrode exhibits a higher activity toward ethanol oxidation in alkaline media than massive Pd electrode. This activity can be ascribed to the particle size and the crystallographic orientation of the palladium trapped in zeolite layer.



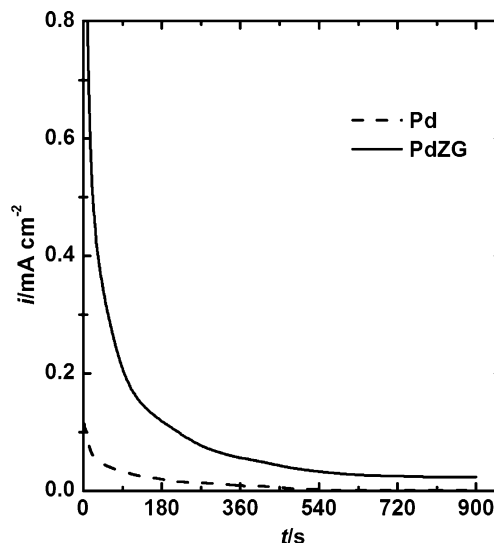
**Fig. 7** Current–peak density/soaking time relationship for PdZG electrode in 0.5 M C<sub>2</sub>H<sub>5</sub>OH+0.5 M NaOH

Moreover, the zeolite–palladium interaction may play an additional rule in activity enhancement. This can be considered as an additional evidence for the electronic interaction.

The voltammograms recorded in ethanol containing solution at three different soaking times in PdCl<sub>2</sub> solution are presented in Fig. 6. The peak current density for ethanol oxidation was found to vary with the soaking time. Figure 7 shows the relationship between the peak current density for ethanol oxidation and the soaking time in Pd<sup>2+</sup> solution. The peak current density was found to increase passing through a maximum at around 20 min soaking time. Beyond this value, the current peak density decreased as the soaking time increased, which may be attributed to the



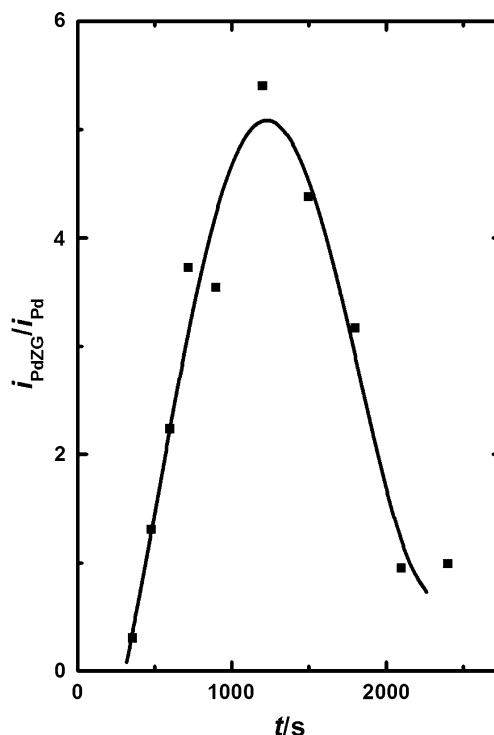
**Fig. 8** Influence of zeolite loading on the current–peak density of ethanol oxidation at PdZG electrodes in sodium hydroxide. Soaking time in PdCl<sub>2</sub> solution=20 min



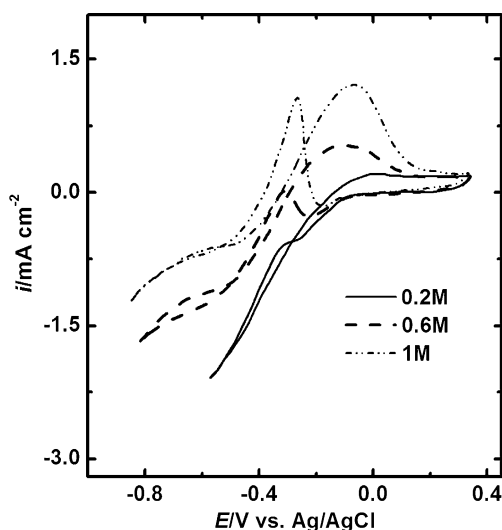
**Fig. 9** Current–time curves for Pd (dashed line) and PdZG (solid line) (presoaked in PdCl<sub>2</sub> for 25 min) electrodes in 0.5 M C<sub>2</sub>H<sub>5</sub>OH+0.5 M NaOH at E=−0.1 V

increase of the Pd particle size. However, the activity is still higher in comparison with massive Pd electrode.

In order to find out the optimum condition for electrode modification, various zeolite loading has been tested. The dependence of current peak density of ethanol oxidation on zeolite loading after immersion in PdCl<sub>2</sub> solution for 20 min has been drawn in Fig. 8. This figure shows that



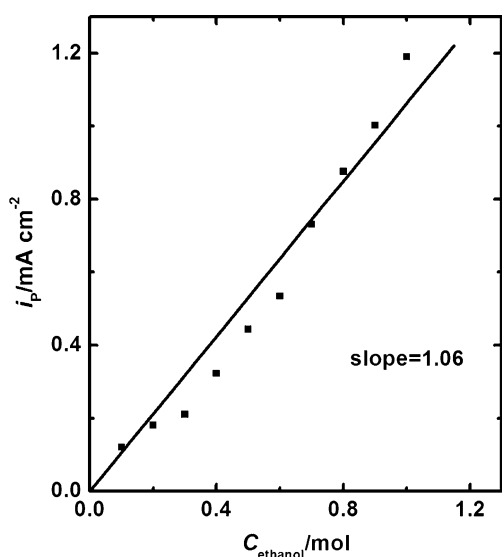
**Fig. 10** Catalytic factor–soaking time relationship for PdZG electrode obtained from *i*–*t* curve recorded at −0.1 V in 0.5 M C<sub>2</sub>H<sub>5</sub>OH+0.5 M NaOH after 15 min



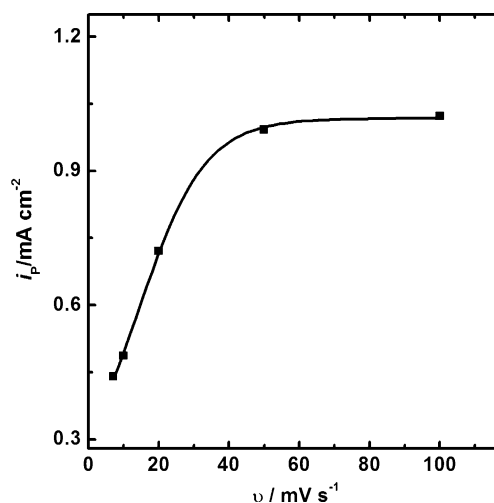
**Fig. 11** Cyclic voltammograms of PdZG electrode in  $xM$   $C_2H_5OH + 0.5$   $NaOH$  (soaking time=12 min in  $PdCl_2$  solution),  $v=50$   $mV s^{-1}$

there is an increase in the oxidation current peak density with the zeolite loading passing through a maximum at zeolite loading equal to 0.024 mg. Increasing the zeolite loading beyond this value leads to a decrease in the oxidation process. This decrease may be attributed to the decrease in the electrode conductivity when zeolites loading exceed a definite value.

The tolerance of the modified electrode against poisoning species was tested using current–decay measurements. Figure 9 shows the comparison between the  $i-t$  curves recorded at  $-0.1$  V (Ag/AgCl) for PdZG and Pd electrodes. As can be seen in this figure, after 15 min of electrolysis in ethanol containing solution, current density falls to approximately zero in case of solid Pd electrode, while a PdZG



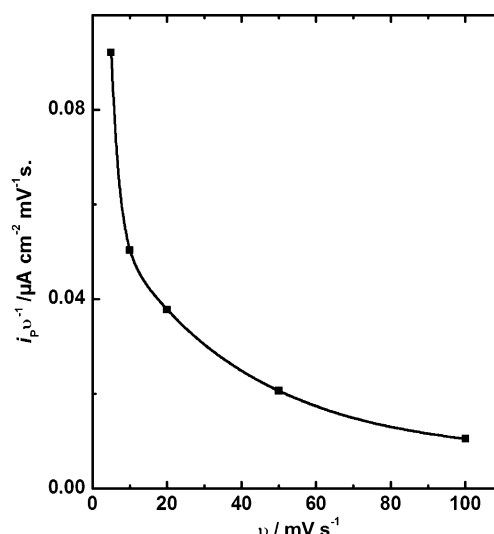
**Fig. 12** Dependence of ethanol oxidation current peak on the ethanol concentration



**Fig. 13**  $i_p-v$  relationship for PdZG electrode in  $0.5$   $M$   $C_2H_5OH + 0.5$   $M$   $NaOH$

electrode soaked for 25 min in  $Pd^{2+}$  solution exhibits around  $23 \mu A cm^{-2}$ . The catalytic activity, obtained by dividing the current density obtained from  $i-t$  curves after 15 min for PdZG electrode by that of Pd one, was drawn against the soaking time for PdZG electrode in Fig. 10. A peak-shaped curve was obtained with a maximum located at 25-min soaking time.

Figure 11 shows the cyclic voltammograms of PdZG electrode in  $0.5$   $M$   $NaOH$  in the presence of different concentrations of ethanol. The peak height was found to increase as the ethanol concentration increase. The data covering the whole concentration range under study are presented in Fig. 12. A straight line passing through the origin, with a slope equal to unity is shown, indicating that the process is purely diffusion controlled.



**Fig. 14** Plot of  $i_p/v$  vs.  $v$  for PdZG electrode in  $0.5$   $M$   $C_2H_5OH + 0.5$   $M$   $NaOH$



The dependence of PdZG electrode activity toward ethanol oxidation on the potential scan rate was clarified. The relationship between peak current density and the scan rate is presented in Fig. 13. The peak current was found to be proportional to the scan rate up to  $20 \text{ mV s}^{-1}$ , showing a normal behavior for a surface adsorbed substance. However, at scan rates  $>20 \text{ mV s}^{-1}$ , deviation from linearity is observed. The ratio between  $i_p/v$  (Fig. 14) was found to decrease with the scan rate ( $v$ ). This indicates that the reaction between palladium particles trapped in zeolite layer and ethanol molecules depends on the rate of diffusion of ethanol through zeolite channels in order to reach the palladium particles. Decreasing the scan rate allows more ethanol molecules to penetrate the zeolite matrix to reach Pd particles leading to higher oxidation rate.

## Conclusion

Zeolite graphite electrode has been modified by Pd using a simple immersion technique. This technique allows the possibility of varying, by a simple way, the amount of noble metal loading and therefore its practical size by changing the soaking time in metal ion solution. PdZG electrodes show a better activity as well as poisoning tolerance during ethanol oxidation in alkaline medium in comparison with Pd electrode. The whole oxidation reaction was found to be a diffusion-controlled process depending on the diffusion of ethanol molecule through the zeolite channels to reach the Pd particles.

## References

1. El-Shafei AA, Abd El-Maksoud SA, Fouda SA (1995) *J Electroanal Chem* 395:181. doi:10.1016/0022-0728(95)04079-4
2. Wang HJ, Yu H, Peng F, Lv P (2006) *Electrochem Commun* 8:499. doi:10.1016/j.elecom.2006.01.019
3. Smant PV, Fernandes JB, Rangel CM, Figueiredo JL (2005) *Catal Today* 102:173. doi:10.1016/j.cattod.2005.02.039
4. Neto AO, Franco EG, Arico E, Linardi M, Gonzalez ER (2003) *J Eur Ceram Soc* 23:2987. doi:10.1016/S0955-2219(03)00310-8
5. Golikand AN, Golabi SM, Maragheh MG, Irannejad L (2005) *J Power Sources* 145:116. doi:10.1016/j.jpowsour.2005.02.061
6. Xue KH, Cai CX, Yang H, Hhou YM, Sun SG, Chen SP, Xu G (1998) *J Power Sources* 75:207. doi:10.1016/S0378-7753(98)00098-6
7. Kitani A, Akashi T, Sugimoto K, Ito S (2001) *Synth Met* 121:1301. doi:10.1016/S0379-6779(00)01522-8
8. Hatchett DW, Wijeratne R, Kinyanjui JM (2006) *J Electroanal Chem* 593:203. doi:10.1016/j.jelechem.2006.04.014
9. Niu L, Li Q, Wei F, Wu S, Liu P, Cao X (2005) *J Electroanal Chem* 578:331. doi:10.1016/j.jelechem.2005.01.014
10. Khalil MW, Abdel Rahim MA, Zimmer A, Hassan HB, Abdel Hameed RM (2005) *J Power Sources* 144:35. doi:10.1016/j.jpowsour.2004.12.014
11. Samant PV, Fernandes JB (2004) *J Power Sources* 125:172. doi:10.1016/j.jpowsour.2003.07.013
12. Delime F, Leger JM, Lamy C (1999) *J Appl Electrochem* 29:1249. doi:10.1023/A:1003788400636
13. Vigier F, Coutanceau C, Perrard A, Belgsir EM, Lamy C (2004) *J Appl Electrochem* 34:439. doi:10.1023/B:JACH.0000016629.98535.ad
14. Luhua J, Sun G, Sun S, Liu J, Tang S, Li H, Zhou B, Xin Q (2005) *Electrochim Acta* 50:5384. doi:10.1016/j.electacta.2005.03.018
15. Colmati F, Antolini E, Gonzalez ER (2006) *J Power Sources* 157:98. doi:10.1016/j.jpowsour.2005.07.087
16. Samant PV, Fernandes JB (2004) *J Power Sources* 125:172. doi:10.1016/j.jpowsour.2003.07.013
17. Chu YH, Ahn SW, Kim DY, Kim HJ, Shul YG, Han H (2006) *Catal Today* 111:176. doi:10.1016/j.cattod.2005.10.022
18. Pang H, Chen J, Yang L, Liu B, Zhong X, Wai X (2008) *J Solid State Electrochem* 12:237. doi:10.1007/s10008-007-0383-4
19. Shen P, Xu CW (2006) *Electrochem Commun* 8:184. doi:10.1016/j.elecom.2005.11.013
20. Xu C, Cheng L, Shen P, Liu Y (2007) *Electrochem Commun* 9:997. doi:10.1016/j.elecom.2006.12.003
21. Song SQ, Tsiakaras P (2006) *Appl Catal B* 63:187. doi:10.1016/j.apcatb.2005.09.018
22. Ouf AM, Abd Elhafeez AM, El-Shafei AA (2008) *J Solid State Electrochem* 12:601. doi:10.1007/s10008-008-0503-9
23. El-Shafei AA (1999) *J Electroanal Chem* 471:89. doi:10.1016/S0022-0728(99)00235-1
24. Rand DA, Woods R (1971) *J Electroanal Chem* 31:29. doi:10.1016/S0022-0728(71)80039-6
25. Jiang YX, Ding N, Sun SG (2004) *J Electroanal Chem* 563:15. doi:10.1016/j.jelechem.2003.08.017
26. Jiang YX, Sun SG, Ding N (2001) *Chem Phys Lett* 344:463
27. Chen ZF, Jiang YX, Wang Y, Xu JM, Jin LY, Sun SG (2005) *J Solid State Electrochem* 9:363
28. Jiang YX, Si D, Chen SP, Sun SG (2006) *Electroanalysis* 18:1173. doi:10.1002/elan.200503501