



Energy conversion using Pt-Pd/C anode catalyst in direct 2-propanol fuel cell

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Abstract: The Pt-Pd/C electrocatalyst was synthesized on graphite substrate by the electrochemical co-deposition technique. The Physico-chemical characterization of the catalyst was done by SEM, XRD and EDX. The electrochemical characterization of the Pt-Pd/C catalyst for 2-propanol electro-oxidation was studied over a range of 2-propanol concentrations in alkaline medium using cyclic voltammetry, chronoamperometry and electrochemical impedance spectroscopy. The activity of 2-propanol oxidation increased with the increase of 2-propanol concentration, at 2-propanol concentration greater than 1.0 M, no change in the oxidation peak current density is because of excess 2-propanol at the electrode surface and/or depletion of OH⁻ at the electrode surface. The Pt-Pd/C catalyst shows good stability and the low value of charge transfer resistance. The enhanced electrocatalytic activity of the electrodes is ascribed to the synergistic effect of higher electrochemical surface area, preferred OH⁻ adsorption and ad-atom contribution on the alloyed surface.

Keywords: 2-propanol; Electro-oxidation; Pt-Pd/C; Electrocatalyst

1 Introduction: Direct alcohol fuel cells (DAFCs) have attracted enormous attention as power sources for portable electronic devices and transportation because liquid alcohol fuels have a higher energy density and are easier to handle and store than hydrogen gas fuel. The DAFCs have several advantages, including low cost, low weight, and simple construction without a reformer. The direct methanol fuel cell (DMFC) is the mostly studied type of DAFC because methanol contains no C-C bond and thus can be relatively easily oxidized completely to CO₂. However, CO poisoning to anode catalysts and the methanol crossover have severely hindered the progress of DMFC developments [1, 2]. At the same time, direct ethanol fuel cells (DEFCs) have attracted more and more attention because ethanol is less toxic compared to methanol and can be easily produced in great quantity by the fermentation of sugar-containing raw materials [3, 4]. However, the ethanol electrooxidation has slow reaction kinetics that is still the main problem for its direct application in an ethanol fuel cell (DEFC). The main problem in achieving an efficient conversion is that the ethanol oxidation reaction occurs through different reaction pathways. In some pathways, large amounts of partially oxidized products are produced due to the difficulty in breaking the C-C bond [5 - 7]. These partially oxidized products do not only decrease the total efficiency of the system, but are also unwanted due to their polluting nature. In other pathways, strongly adsorbed species are formed, which poison the catalyst surface [7, 8]. 2-propanol (or isopropanol) being the smallest secondary alcohol enjoys the advantage over methanol and ethanol that it does not dissociate into CO at the electrode surface. In addition, being a bulky molecule it is less prone to crossover, through ion-exchange membrane than methanol and ethanol, causing least cathode poisoning [9 - 12]. The direct 2-propanol fuel cell (D2PFC) shows better performance than DMFCs and a much lower crossover current [13]. Qi and Kaufman

[10] and Cao and Bergens [13] have demonstrated that the acidic D2PFC has higher working voltage and higher power density than DMFC, particularly at current densities lower than 200 mA cm^{-2} . However, they also found that the cell voltage of D2PFC dropped rapidly if operating at high current density or for a long time. Recently, more attentions have been given to alkaline D2PFC, which is expected to have a higher performance than its acid counterpart because electro-oxidation of alcohol and electroreduction of oxygen have faster kinetics in alkaline medium than in acid medium and non-noble metals can be used as anode catalyst [14, 15]. Unlike electrooxidation of methanol, which generates CO_2 as the product and will react with alkaline electrolyte, the electro-oxidation of 2-propanol only produce acetone at low overpotential independent on the nature of electrocatalysts [16, 17], therefore alkaline electrolyte can be used in D2PFC. Very recently, Markiewicz and Bergens [18] showed that the alkaline D2PAFC significantly outperformed the alkaline DMFC. As to the electrocatalysts for 2-propanol oxidation in alkaline electrolytes, several noble metals, including Pt, Pd, Ru, Au, Pt–Ru, Pt–Au, Pd–Au, have been demonstrated to be effective candidates [19–22]. The work in this paper entails a comprehensive study on the physicochemical as well as electrochemical characterization of the synthesized Pt-Pd/C electrode towards oxidation of isopropanol in NaOH media. For physicochemical characterization, different techniques like scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) study were employed. Electrochemical techniques like voltammetry, chronoamperometry, and electrochemical impedance spectroscopy (EIS) were used to derive the electrocatalytic behavior of the electrodes towards 2-propanol oxidation.

2. Materials and methods:

Electrochemical deposition of Pt and Pd or co-deposition of Pt and Pd were made on coupons of graphite samples with surface area of 0.65 cm^2 . Electrodeposition of Pt and Pd were carried out using $0.05 \text{ M H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and 0.05 M PdCl_2 solutions respectively. Both $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and PdCl_2 solutions were prepared in 2.0 M HCl and Milli-Q water. For electrochemical co-deposition of Pt and Pd, an equimolar mixture of $0.05 \text{ M H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and 0.05 M PdCl_2 was used. For each case electrodeposition was performed at room temperature under galvanostatic control by applying 5 mA cm^{-2} current with the help of computer controlled PG Stat (AUTOLAB 30) for certain duration. Catalyst loading for each electrode was maintained at 0.5 mg cm^{-2} . Bulk composition of the Pt-Pd/C electrocatalyst was determined by energy dispersive X-ray spectroscopy (EDX) while scanning electron microscopy (SEM) was employed to reveal the surface morphology. All these measurements were done with a JSM-6700F FESEM at an accelerating potential of 5 kV . In order to obtain information about the surface and bulk structure of the catalyst, X-ray diffraction (XRD) study was carried out with the help of Philips PW 1140 parallel beam X-ray diffractometer with Bragg-Bretano focusing geometry and monochromatic $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). Electrochemical measurements like cyclic voltammetry and chronoamperometry were carried out in the standard three-electrode cell at different temperature with the help of computer controlled AUTOLAB 30 Potentiostat/Galvanostat from Ecochemie B.V., The Netherlands. The working solutions were deaerated by purging with nitrogen (XL grade). Electrochemical impedance spectroscopy studies were conducted using the same AUTOLAB 30 PGSTAT with a frequency response analyzer (FRA) module. EIS was performed with amplitude of 5 mV for frequencies ranging from 40 kHz to 100 mHz . Each scan contained about 100 data points (20 data points per decade). The impedance spectra were fitted to an equivalent circuit model using a non-linear fitting program. A mercury-mercuric oxide (MMO) reference electrode and a platinum foil ($2 \times 1 \text{ cm}^2$) counter electrode were used for all electrochemical experiments. All the potential in this paper are referenced to the standard hydrogen electrode (SHE) at cell operating temperature and the current is normalized to the geometrical surface area.

3. Results and discussion:

The morphologies of the catalyst surface were studied using scanning electron microscopy. Pt-Pd particles show better dispersion than Pt on the graphite substrate shown in Figure (1). As platinum and

palladium were co-electrodeposited on the graphite surface both the metals were grown together on the same sphere making an assembly of ad-atoms in the form of agglomerated particles. The size of the particles does not show much variation and were found to remain within the range of (80-100 nm).

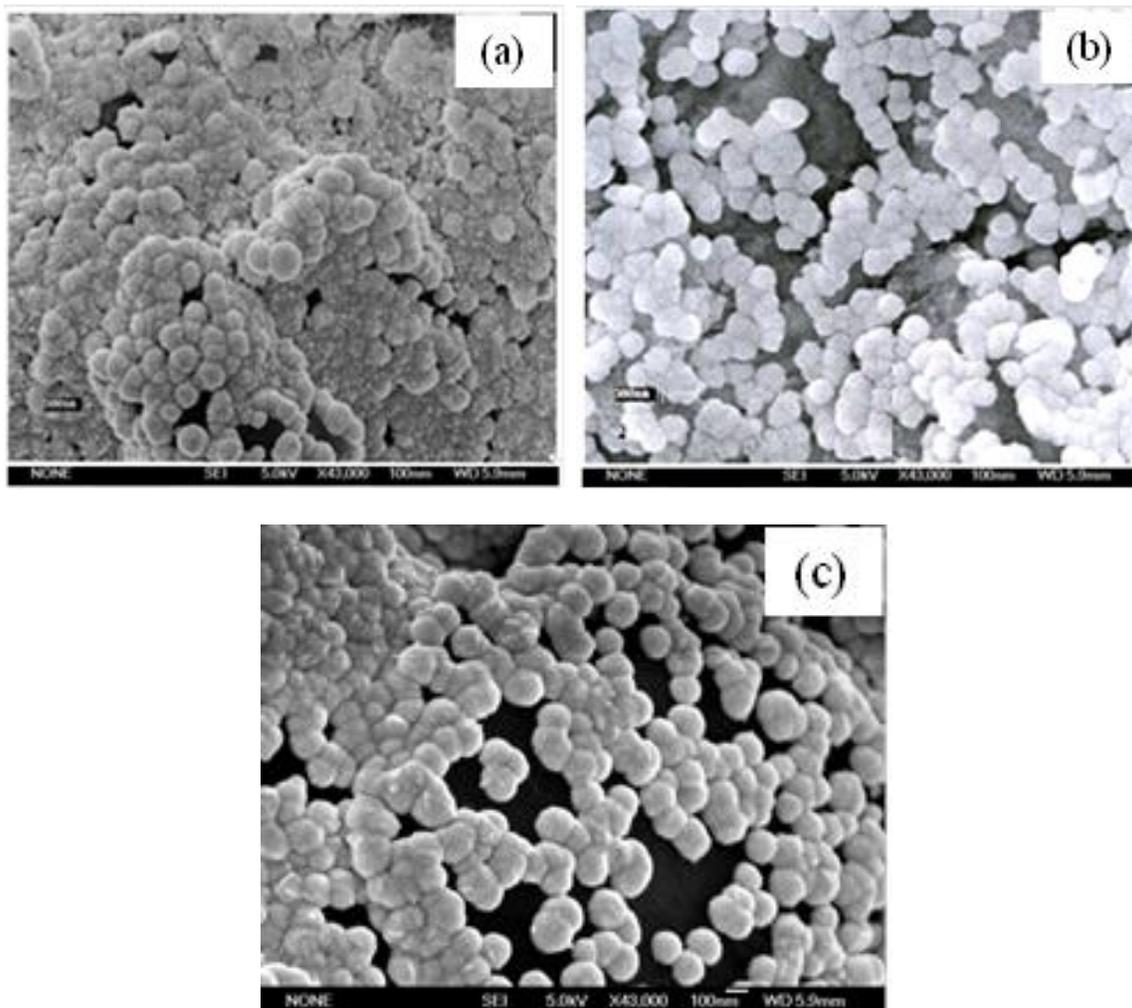


Figure (1): Scanning electron micrographs of (a) Pt/C, (b) Pd/C and (c) Pt-Pd/C catalysts.

The Pt and Pd nanoparticles co-electrodeposited on graphite surface exhibited an XRD pattern of a typical face-centered-cubic lattice structure as shown in Figure (2). The strong diffraction peaks at the Bragg angles of 40.08° , 46.67° , 68.02° , 82.08° and 86.45° correspond to the (111), (200), (220), (311) and (222) facets of Pt-Pd crystal. Alloying of Pt and Pd does not change the diffraction pattern. With the incorporation of Pd into the fcc structure of Pt, the diffraction peaks were shifted to higher values of 2θ , which is indicative of contraction of lattice. No characteristic peaks of Pt or Pd oxides were detected. The (111) peak was used to calculate the particle size of the Pt-Pd crystal according to the Debye-Scherrer equation. The average particle size in the Pt-Pd/C catalyst matrix was found to be 6.5 nm. However, the morphology indicated agglomeration of smaller particles throughout the matrix. The bulk compositions of electrocatalysts were investigated using energy dispersive X-ray spectroscopy (EDX) and atomic ratio of Pt to Pd was found to be 1:2. The electrocatalytic activity of Pt/C, Pd/C and co-deposited Pt-Pd/C electrodes towards the oxidation of 2-propanol was investigated. The voltammograms for the solution containing 1.0 M of 2-propanol and 0.5 M NaOH are shown in Figure (3). The shapes of the voltammograms are similar for all the three electrocatalysts. The anodic sweep consists of hydride region as well as 2-propanol oxidation region, which actually overshadows the oxide formation region.

In the cathodic sweep oxide reduction region is discernible followed by a reverse oxidation peak and the hydride region. However, the reverse oxidation peak is also quite prominent for Pt-Pd/C.

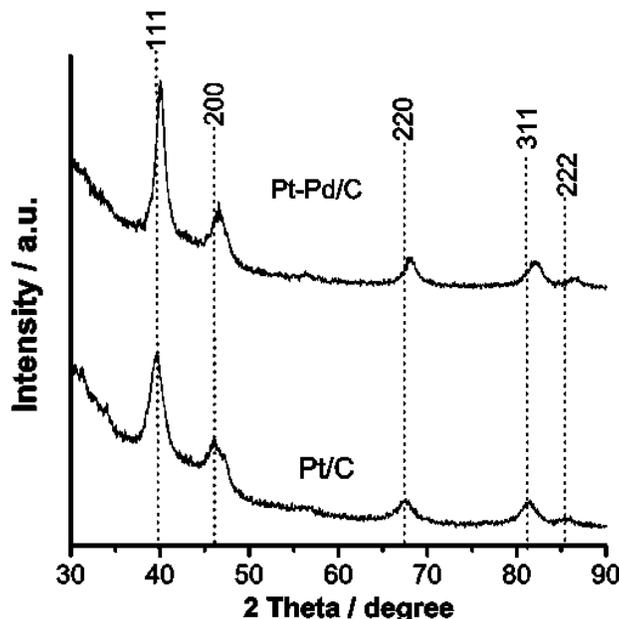


Figure (2): X-ray diffraction pattern of Pt/C and Pt-Pd/C electrocatalysts.

The rapid increase in current during the cathodic sweep shows that the surface oxide formed may impede the electro-oxidation [23]. In case of Pt/C electrode, 2-propanol oxidation current density reaches its maximum in alkaline medium with a magnitude of 89 mA cm^{-2} , while Pd/C electrode yielded lower current density of 43 mA cm^{-2} . For the binary Pt-Pd/C electrode oxidation current density attained a far high value of 136 mA cm^{-2} . A positive shift in oxidation peak potential (E_p) from Pd/C (135 mV) to Pt/C (389 mV) and Pt-Pd/C (508 mV) was however observed. The onset for the oxidation reaction was observed at -801 mV for Pt-Pd/C electrode, -785 mV for Pt/C and -785 mV for Pd/C as depicted in Figure (3).

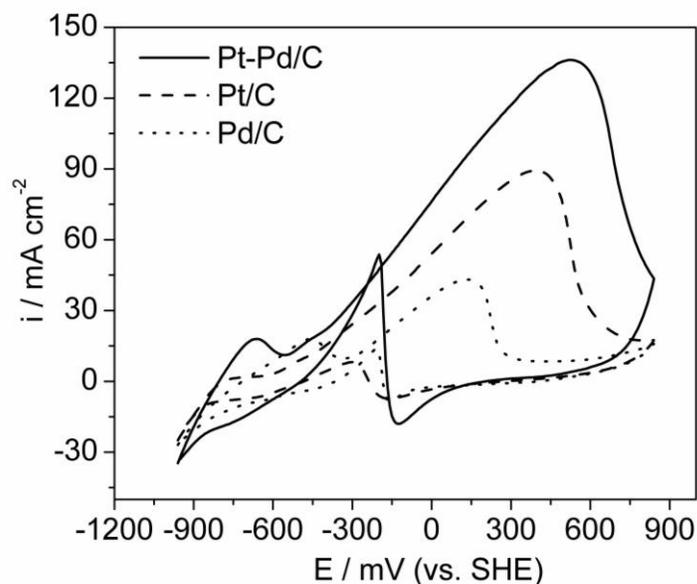


Figure (3): Cyclic voltammograms for 2-propanol oxidation on Pt/C, Pd/C and Pt-Pd/C electrodes in a mixture of 0.5 M NaOH and 1.0 M 2-propanol. Sweep rate: 50 mV s^{-1} .

All these parameters project that Pt-Pd/C can serve as a fairly good catalyst for electro-oxidation of 2-propanol in alkaline media. In case of 2-propanol, the surface adsorption of the bulky alcohol molecule is difficult from the point of steric hindrance. Under this effect the oxidation reaction can propagate only with moderate concentration of 2-propanol. Supposedly high concentration of the alcohol leads to concentration polarization of the electrode due to formation of bulky intermediates, which reduces the number of active sites. The prime reaction occurring at the electrode in alkaline media is the dehydrogenation of 2-propanol to acetone, i.e.

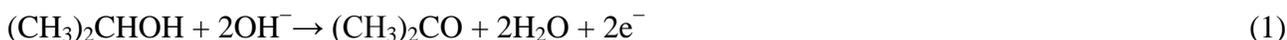


Figure (4) shows the effect of varying the 2-propanol concentration on the linear sweep voltammograms for 2-propanol oxidation at a fixed NaOH concentration of 0.5 M. Attempts to use higher concentrations of 2-propanol (> 2.0 M) was prevented due to the formation of biphasic electrolyte mixture. Increase in the concentration of 2-propanol resulted in an increase in the current in the hydride, double layer and oxide regions of the voltammograms however, anodic shift in the current maxima is also observed. The shape of the voltammograms did not change significantly upon increasing the 2-propanol concentration. This behavior may be explained by a shift from a diffusion-controlled reaction at low 2-propanol concentrations to quasi activation control wherein the insufficient availability of OH^- , disproportionate to the 2-propanol concentration, inhibit the oxidation reaction due to the adsorbed intermediates produced at higher concentrations. The variation of onset potentials for oxidation of 2-propanol with its concentration is shown in Table I. A cathodic shift of onset potential was observed up to 2-propanol concentration of 1.0 M and beyond which the value becomes steady. At much higher concentrations the adsorption of alcohol molecules dominates and prevents the adsorption of OH^- ions and thus the onset potential become invariant. The reaction order with respect to the alcohol was determined by plotting $\log i$ vs. $\log [2\text{-PrOH}]$ at given points in the low potential range, shown in Figure (5). The electro-oxidation of 2-propanol did not show linear behavior throughout the concentration range in the polarization plot.

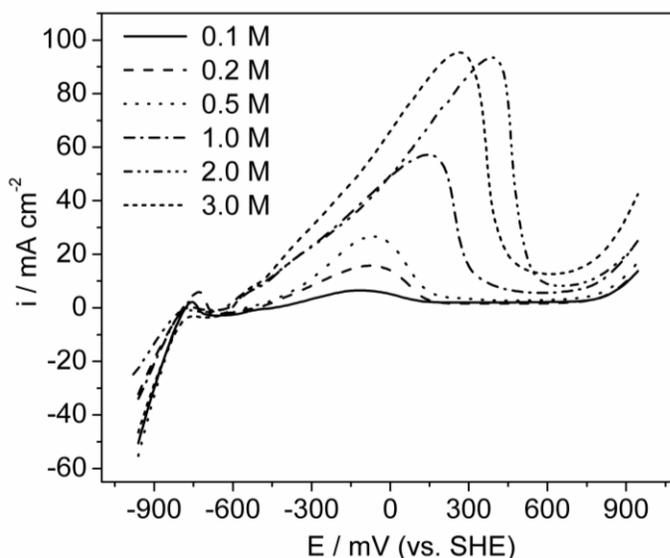


Figure (4): Linear sweep voltammograms for 2-propanol oxidation on Pt-Pd/C electrodes in 0.5 M NaOH at various 2-propanol concentrations. Sweep rate: 1.0 mV s^{-1} .

The 2-propanol is characterized by non-uniform reaction order in the cathodic as well as in the anodic potentials. In the concentration range (0.1–1.0 M) at lower potentials there is scarcity of alcohol molecule adsorbed on to the surface that translates to poor oxidation kinetics and a reaction order of 0.2 was obtained for 2-propanol. However at higher concentration of 2-propanol and at higher potential,

improved oxidation rate is observed with higher order (0.8) with respect to alcohol till the mechanism gets more complicated. However, the overall kinetics of 2-propanol oxidation seems to be catalytically favored on Pt-Pd/C electrode in alkaline medium as reflected by the considerable lowering of the onset potentials. The long-term stabilities of Pt-Pd/C electrode for 2-propanol oxidation were investigated with chronoamperometric techniques. The concentration dependence of the current density for 2-propanol oxidation was measured at a constant potential of -160 mV. Chronoamperometric curves, obtained after applying a potential -160 mV for 1000 seconds in 0.5 M NaOH solution, with various concentrations of 2-propanol are shown in Figure (6). The rapid current decay shows the poisoning for the electrocatalysts. At any time, oxidation current does not show much increase with the increase in concentration of 2-propanol.

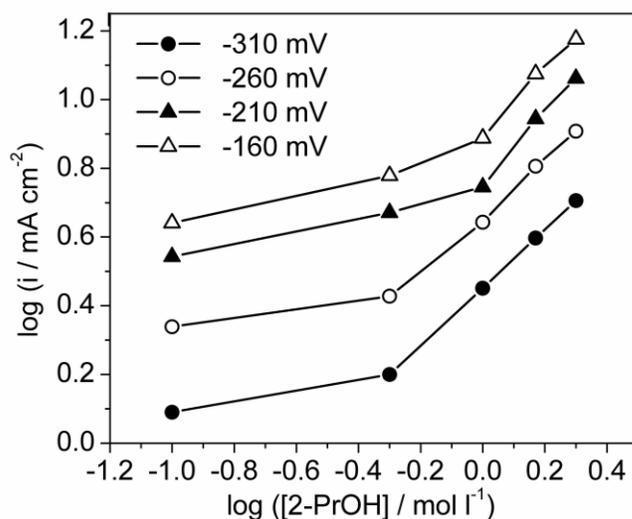


Figure (5): Dependence of 2-propanol oxidation rate on 2-propanol concentration in 0.5 M NaOH solution.

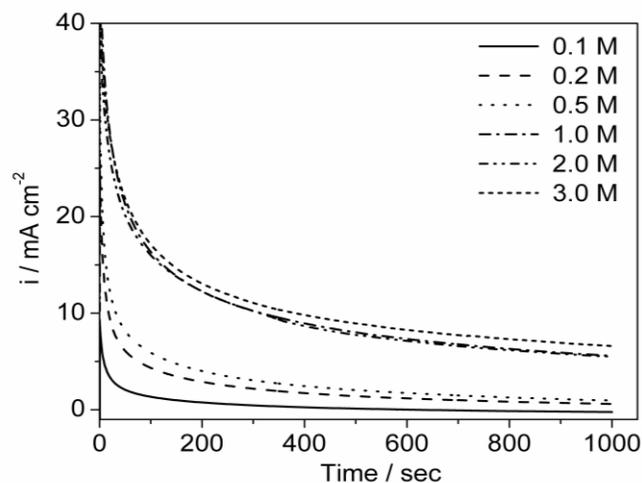


Figure (6): Chronoamperometric curves for 2-propanol oxidation at -160 mV (vs. SHE) on Pt-Pd/C electrode in 0.5 M NaOH containing various concentration of 2-propanol.

The initial rapid current decay can be addressed to a considerable increase in the surface coverage with the partially oxidized intermediates produced from the oxidation of 2-propanol. The long-term poisoning rate (δ) was calculated from Figure (7) by using equation (2).

$$\delta = \frac{100}{i_0} \times \left(\frac{di}{dt} \right)_{t > 500 \text{ sec}} \quad (\% \text{ per sec}) \quad (2)$$

where $(di/dt)_{t > 500 \text{ sec}}$ is the slope of the linear portion of the current decay and i_0 is the current at the start of polarization back extrapolated from the linear current decay. The calculated δ values are presented in Table (1). Although the long-term poisoning rates have the highest value for 0.1 M 2-propanol, it decreases with the increase in concentration of 2-propanol. Electrochemical impedance spectroscopic (EIS) study enabled to dissect the various impedance parameters for the charge transfer reaction occurring across the electrode solution interface. Nyquist plots for 2-propanol oxidation in a solution containing 0.5 M NaOH and 1.0 M 2-propanol at 25⁰C are shown in Figure (7). In the lower potential region the Nyquist plot showed a capacitive feature due to the hydrogen adsorption/desorption and double layer charging/discharging. In the Tafel region, ($-310 \text{ mV} < E < -160 \text{ mV}$) the Nyquist plot tends towards forming semi-circles.

Table (1): the onset potentials and long-term poisoning rate on the Pt-Pd/C electrode surface for electro-oxidation of 2-propanol.

2-propanol concentration (M)	Onset potentials (mV)	Poisoning rate (δ % per sec)
0.1	-444.3	0.160
0.2	-507.7	0.075
0.5	-547.4	0.069
1.0	-610.9	0.047
2.0	-603.0	0.045
3.0	-603.0	0.041

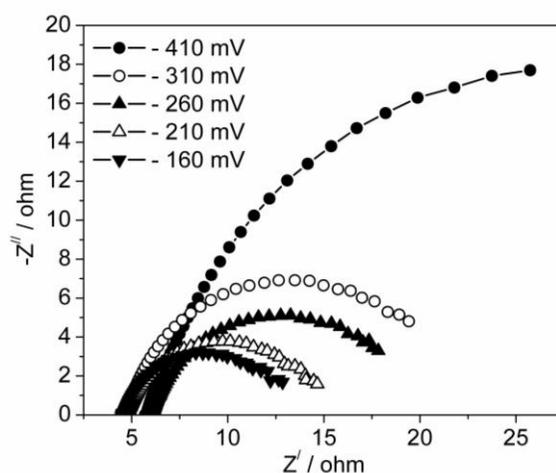


Figure (7): Impedance spectra for 2-propanol oxidation on Pt-Pd/C electrode at different potentials in a mixture of 0.5 M NaOH and 1.0 M 2-propanol, at 25⁰C.

The charge transfer resistance derived from the Nyquist plot was related to the potential within this region. The charge transfer resistance (R_{ct}) decreased with increasing potential, indicating that charge transfer propensity increases with potential. The double layer capacitance was expressed in terms of a constant phase elements (CPE). An equivalent circuit for the EIS is suggested in Figure (8).

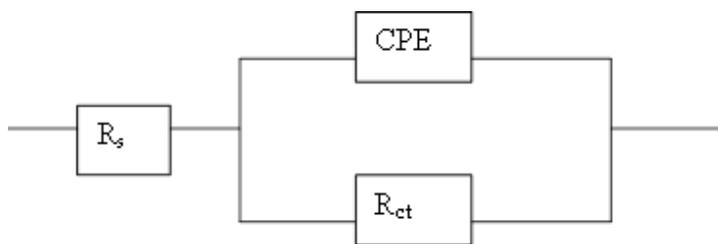


Figure (8): Proposed equivalent circuits for the 2-propanol oxidation on Pt-Pd/C electrode in a mixture of 0.5 M NaOH and 1.0 M 2-propanol at 25 °C.

The calculated impedance parameters are listed in Table (2). The high values of charge transfer resistance and double layer capacitance are indicative of poor kinetics of 2-propanol oxidation and difficulty of desorption of the reaction intermediates.

Table (2): calculated impedance parameters from the equivalent circuit at -260 mV (vs. SHE) for 2-propanol oxidation on the Pt-Pd/C electrode.

Solution resistance, R_s (ohm)	CPE (mF)	R_{ct} (ohm)
6.18	8.82	13.80

4. Conclusions: The outcome of this study reveals that Pt-Pd/C is a fairly good electrocatalyst for 2-propanol oxidation in alkaline medium. The most encouraging result obtained with Pt-Pd/C catalyst is the considerable lowering of over-potential in alkaline medium when compared with the other alcohols studied. Voltammetry and EIS studies have been used to investigate the kinetics of 2-propanol oxidation in NaOH media on the Pt-Pd/C electrode. The kinetics of the 2-propanol oxidation reaction on the electrode is enhanced with the increase in concentration of 2-propanol. The reaction order for 2-propanol depends on the concentration range of 2-propanol and suggests different reaction mechanism at low and high concentration of 2-propanol. The results also show that use of the Pd with Pt increases the electrocatalytic activity towards 2-propanol oxidation in alkaline medium as well as reduces the amount of expensive Pt in the electrode material.

References:

- [1] S-W Xie, S. Chen, Z-Q Liu, C-W Xu, *Int. J. Electrochem. Sci.* 6 (2011) 882.
- [2] S. P. Jiang, Z. C. Liu, Z. Q. Tian, *Adv. Mater.* 18 (2006) 1068.
- [3] L.D. Zhu, T.S. Zhao, J.B. Xu, Z.X. Liang, *J. Power Sources* 187 (2009) 80.
- [4] G.C. Li, P.G. Pickup, *J. Power Sources* 161 (2006) 256.
- [5] G. A. Camara, T. Iwasita, *J. Electroanal. Chem.* 578 (2005) 315.
- [6] H. Wang, Z. Jusys R. J. Behm, *J. Phys. Chem. B* 108 (2004) 19413.
- [7] D. J. Tarnowski C. Korzeniewski, *J. Phys. Chem. B* 101 (1997) 253.
- [8] T. Iwasita E. Pastor, *Electrochim. Acta* 39 (1994) 531.
- [9] C-G. Lee, M. Umeda, I. Uchida, *J. Power Sources* 160 (2006) 78.
- [10] Z. Qi, A. Kaufman, *J. Power Sources* 118 (2003) 54.
- [11] S. Rousseau, C. Coutanceau, C. Lamy, J.M. Leger, *J. Power Sources* 158 (2006) 18.
- [12] E. Hao Yu, K. Scott, R.W. Reeve, L. Yang, R.G. Allen, *Electrochim. Acta* 49 (2004) 2443.
- [13] D.X. Cao, S.H. Bergens, *J. Power Sources* 124 (2003) 12.
- [14] J. Lu, S. Lu, D. Wang, M. Yang, Z. Liu, C. Xu, S.P. Jiang, *Electrochim. Acta* 54 (2009) 5486.

- [15] E.H. Yu, K. Scott, R.W. Reeve, J. Electroanal. Chem. 547 (2003) 17.
- [16] A. Santasalo-Aarnio, Y. Kwon, E. Ahlberg, K. Kontturi, T. Kallio, M.T.M. Koper, Electrochem. Commun. 13 (2011) 466.
- [17] I.A. Rodrigues, F.C. Nart, J. Electroanal. Chem. 590 (2006) 145.
- [18] M.E.P. Markiewicz, S.H. Bergens, J. Power Sources 195 (2010) 7196.
- [19] C. Xu, Z. Tian, Z. Chen, S.P. Jiang, Electrochem. Commun. 10 (2008) 246.
- [20] Y. Su, C. Xu, J. Liu, Z. Liu, J. Power Sources 194 (2009) 295.
- [21] W. Zhou, C. Wang, J. Xu, Y. Du, P. Yang, Mater. Chem. Phys. 123 (2010) 390.
- [22] F.J. Santasalo, I. Vidal, J. Solla-Gull, A. Bern, T. Kallio, J.M. Feliu, Electrochim. Acta 54 (2009) 6576.
- [23] J. Otomo, X. Li, T. Kobayashi, C. Wen, H. Nagamoto, H. Takahashi, J. Electroanal. Chem. 573 (2004) 99.
