

Ceria Based Nano-composite Synthesis for Direct Alcohol Fuel Cells

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Ethanol electro-oxidation activities of electrocatalysts for direct alcohol fuel cells (DAFC), prepared by impregnation-hydrothermal method were investigated by cyclic voltammetry, chronoamperometry, chronopotentiometry and fuel cell tests. In addition, the relation between activity and morphology, chemical and physical structure were determined by spectroscopic techniques. X-ray photoelectron spectroscopy showed that the surface oxygen content of electrocatalysts can be arranged in order as: Pt/NiCeOx> Pt/PdCeOx>Pd/PtCeOx> Ni/PtCeOx> Pt/FeCeOx> Fe/PtCeOx. Comparison of XPS and ICP-OES (bulk and surface analysis) indicate that; after hydrogen reduction Pt and Ni in Pt/NiCeOx or Ni/PtCeOx segregate to the surface. The same behavior was also seen for Pt and Pd in Pt/PdCeOx or Pd/PtCeOx. However, in the case of Pt and Fe, surface segregation of Fe is higher than Pt. Diffraction analysis show that, after hydrothermal synthesis, Fe was in the form of Fe₃O₄ in the support phase but Pt and Ni may incorporate into the ceria matrix. Although metallic Pt, Pd and Ni are seen in ceria phase, Fe and Ni may also appear as a different oxide phase (Fe₂O₃ or NiO) beside ceria. Both XRD and TEM analysis support the existence of Fe and Ni oxides. Cyclic voltammograms indicate that all home made catalysts exhibit typical ethanol electro-oxidation peaks, magnitudes of oxidation current densities can be arranged in order as Fe/PtCeOx> Pt/PdCeOx>PtRu/C. When anodic polarizations at 0.5 mA are compared from lowest to highest, it was seen that, Fe/PtCeOx< Pt/PdCeOx<PtRu/C <Pd/PtCeOx. At constant potential of 0.6V, highest steady state currents were achieved for Fe/PtCeOx. Steady state currents can be shown as in order: Fe/PtCeOx>Pd/PtCeOx>PtRu/C ≈ Pt/PdCeOx. Although, power densities of home-made electro-catalysts are close to that of commercial PtRu/C at 40°C, because of the intense kinetic effect in PtRu/C, the performances of home-made electro-catalysts fall behind PtRu/C at 60 and 80°C. After physically mixing home-made electro-catalysts with the commercial PtRu/C, fuel cell performances drastically improved and even higher power densities than PtRu/C could be obtained for Ni/PtCeOx+PtRu/C, Pt/FeCeOx+PtRu/C and Pt/PdCeOx+PtRu/C.

Keywords: Ethanol, Electro-oxidation, Electrocatalyst, Hydrothermal, Ceria, Synthesis, Fuel cell

1. INTRODUCTION

Nano-structures as in the case of cerium oxide exhibit different functional and electrocatalytic properties by modification of their geometric shapes to polyhedra, nano-rod or nano-cube during anisotropic growth of crystal structure by hydrothermal technique. The reason why the hydrothermal route is generally preferred is that the temperature, acidity, concentration and reaction time can be easily adjusted for the desired nano-structure. Moreover, high oxygen storage capacity, high oxygen mobility and high CO oxidation rate of these ceria based nano-structures make them suitable candidates as anode materials in direct ethanol fuel cells [1-6]. Another reason for the use of ceria may be the chemical oxidation studies of methanol on certain nano-structures that can decompose methanol into methoxy and formate and can increase CO₂ formation due to their specific valance oxidation state.

Superior properties of CeO₂ and transition metal loaded CeO₂ prepared by different techniques like impregnation, colloidal and micro-emulsion are also pronounced frequently in the literature [7-13]. For instance, it was seen that uniform Pt-CeO₂ particles on carbon support improve methanol electro-oxidation activity by the drop of onset potential and increase in oxidation current [12]; in addition, like in the case of bi-metallic alloys in order to optimize electro-catalytic activity, the amount of CeO₂ can be adjusted in the catalyst. For instance, CeO₂ can be a substitute for Ru in PtRu/C electrocatalyst. When ceria was applied instead of PtRu/C in direct methanol fuel cell, it was seen that optimum amount of CeO₂ in Pt-CeO₂/C can lead to lower charge transfer resistance, higher stability and higher peak oxidation currents compared to Pt/C [14]. And other than as a substitute, CeO₂ can also be used with PtRu bimetallics by improved deposition techniques to increase methanol decomposition to CO₂ [15-24].

Incorporation of transition metal into the structure of ceria is another important factor which determines its electrocatalytic activity (e.g. CO electro-oxidation). For instance addition of Pt into the structure of CeO₂ makes Ce⁺⁴ regenerative and causes reversible redox reactions between Ce⁺⁴ and Ce⁺³. What explains the high electrocatalytic activity on these stable structures is the improved electron transfer mechanism from Pt to Ce cations during CO₂ formation [25]. Although several explanations are given about the electronic and bifunctional mechanism, complex electrochemical oxidation scheme of alcohols on ceria based catalysts is still a subject of debate [26]. Other than platinum, different transition metals like Fe can also be doped into ceria structure as a capping agent in order to obtain more improved ceria geometric structures [26, 27].

In this study, in order to prepare nano-composite electrocatalysts, different transition metals like Fe, Ni, and Pt will be doped during hydrothermal synthesis of cerium oxide or will be impregnated after hydrothermal synthesis of transition metal doped cerium oxide. Hydrothermal synthesis procedure was selected because of the ease of application as mentioned above. Fe and Ni non-noble metals that were used during hydrothermal synthesis and impregnation were selected based on their similar chemical and electronic properties to the model PtRu catalyst [28, 29].

It is widely seen in the literature that second or third transition metal and support oxide phase can be used beside Pt in order to increase alcohol electro-oxidation activity. For instance, when Ni is used beside Pt, it was clearly understood that NiO, Ni(OH)₂ or NiOOH can oxidize CO and ethanolic residues by bifunctional mechanism and inhibit bulk metal corrosion. These improvements can be

observed by high current densities, lower onset potentials during cyclic voltammetry and chronoamperometry [30, 31].

2. EXPERIMENTAL

2.1 Catalyst Preparation

Catalysts were prepared in two steps: In the first step, ceria support was prepared by hydrothermal synthesis. In the second step, transition metals were loaded onto the support (maximum 10 weight %) by incipient wetness technique.

2.1.1 Hydrothermal Synthesis

In order to prepare support material by hydrothermal synthesis, ideally 50 wt% CeO₂ and 50 wt % transition metal were taken as a basis in the support. Initially, 1.6 gr ammonium cerium nitrate (NH₄(Ce(NO₃)₆) (Merck Inc.) was dissolved in 5ml deionized water. After that, 6M, 35 ml NaOH solution was added to the dissolved cerium salt. After the solution was stirred on a magnetic stirrer for 30 minutes, transition metal salt (PtCl₄, NiCl₂.6H₂O, Pd(NO₃)₂.2H₂O, Fe(NO₃)₃.9H₂O) (Merck Inc.) (50 wt % metal was taken as a basis) which was dissolved in deionized water previously was added to the mixture and the final solution was stirred for another 30 minutes. Then the final solution was transferred to the sealed autoclave with a Teflon lining and placed in a furnace. Hydrothermal synthesis was carried out at 100°C and 24 hours. After synthesis, the product was washed and filtered with water and ethanol several times and finally dried at 60°C for 12 hours.

2.1.2 Wet Impregnation

In the wet impregnation technique, first of all, metal salts that will be loaded on the support (PtCl₄, NiCl₂.6H₂O, Fe (NO₃)₃.9H₂O, Pd(NO₃)₂.2H₂O) were dissolved in ammonia solution and mixed on a magnetic stirrer for 1 hour. After that, desired amount of cerium composite support was added to the salt solution and mixed at room temperature for 3 hours. Final solution was washed and filtered with deionized water and the precipitate was dried at 100°C overnight. After each synthesis process, targeted amount of catalyst and loading weight percentage were 1 gr and 10 % respectively.

2.1.3 Catalyst reduction

After synthesis, approximately 1 gr of catalyst was reduced under hydrogen atmosphere, at 400°C for 2 hours in a tubular furnace and left to cool down by natural convection. Furnace temperature was increased at a ramp rate of 10°C/min until 400°C. The reduction temperature was

selected based on the surface activation and surface oxygen removal of ceria and PtO_2 reduction [32-39].

2.2 Characterization Studies

2.2.1 Induced Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

In order to determine metallic weight percentages in the bulk home-made catalysts, ICP-OES analysis was performed in METU Central Lab. Perkin Elmer Optima 4300DV model equipment was used for bulk analysis. Emission signals were measured by Echellepolychromator and S-CCD sequential detector system.

2.2.2 X-Ray Photoelectron Spectroscopy (XPS)

XPS studies were carried out by SPECS EA 300 equipped with argon ion gun and Al monochromatic anode. All the partial scans were done after 5 min 3keV Ar ion bombardment. During partial scans, orbital peaks shown in Table 1 were examined in detail.

Table 1. Binding Energies of Orbital Peaks

Binding Energy (eV)			
Orbital	$\text{Ce}^{+3[25,40]}$	$\text{Ce}^{+4[25,40]}$	
Ce 3d 5/2	885,4 881.1	882,6 889,6(satellite) 898,7(satellite)	
Ce3d 3/2	905 904	901,1 908,1(satellite) 917,1(satellite)	
Orbital	$\text{Ni}^{+2[38,39,40]}$	$\text{Ni}^{0[38,39,40]}$	
Ni 2p3/2	854,6	852,6	
Ni 2p1/2	881.8	870.01	
Orbital	$\text{Pt}^{0[25,40]}$	$\text{Pt}^{+2[25,40]}$	$\text{Pt}^{+4[25,40]}$
Pt 4f 7/2	71,1	72,4	74,7
Pt 4f 5/2	74,4	75,7	78
Orbital	$\text{Fe}^{+2[40,41,42]}$	$\text{Fe}^{+3[40,41,42]}$	$\text{Fe}^{+4[40,41,42]}$
Fe 2p1/2	722	718.1	
Fe 2p3/2	709	710.2	706.5
Orbital	$\text{Pd}^{0[40,43,44]}$	$\text{Pd}^{+2[40,43,44]}$	
Pd 3d3/2	340,2(pure Pd) 343,3(in CeO_2 matrice)	343(1%Pd/ CeO_2) 341,6(purePdO)	
Pd 3d5/2	335,4 (purePd) 335,2(1%Pd/ CeO_2) 338,2(in CeO_2 matrice)	336,8(pure PdO) 337,9(1%Pd/ CeO_2)	

2.2.3 X-Ray Diffraction (XRD)

XRD analysis of catalysts were performed by RigakuUltima-IV X-Ray Diffractometer. Scan range was 2 to 120° and scan rate was 1°/min. In order to determine diffraction peaks, in addition to the data from literature [45-51], JCPDS card no: 88-0315, JCPDS card no: 86-2316, JCPDS card no:87-0721 were used for iron and iron oxides, JIPDS card no: 00-034-0394 was used for ceria, JCPDS card no: 4-850 was used for nickel and nickel oxide, JCPDS-ICDD card no: 2000, 87-646 and 01-1194 were used for platinum, JCPDS card no:05-0681 was used for palladium.

2.2.4 Transmission Electron Microscopy (TEM)

TEM analysis were performed by Jeol 2100 HRTEM and Orius SC1000 Model 832 11 Megapixel CCD camera. Before analysis, catalyst powder samples were dispersed in ethanol in ultrasonic bath for 30 min and the suspension was injected on HC300-Cu Holey Carbon Mesh and CF300-Cu Carbon Film and dried overnight.

2.2.5 Scanning Electron Microscopy (SEM)

Surface morphology of home-made catalysts were analyzed by QUANTA – 400F Model electron microscopy with a 1.2 nm resolution.

2.3 Electrochemical Analysis

Three different electrochemical techniques were applied to compare the electrochemical performances of home-made electrocatalysts.

2.3.1 Cyclic Voltammetry, Chronoamperometry and Chronopotentiometry

Three electrode cell was used for cyclic voltammetry, chronoamperometry and chronopotentiometry. In this electrochemical cell, working electrode (WE) was a glassy carbon (that has a surface area of 0.196 cm²) loaded with 10 mg electrocatalyst and 10 µl Nafion solution binder. Reference electrode was standard calomel electrode (SCE) (0.242V vs. Reversible Hydrogen Electrode (RHE)). The counter electrode was platinum wire electrode separated from the cell by a coarse frit. 0.5M H₂SO₄ + 0.5M C₂H₅OH solution was used as an electrolyte in the electrochemical cell. In order to perform cyclic voltammetry, chronoamperometry and chronopotentiometry analysis, computer controlled Gamry Reference 600 Potentiostat/Galvanostat was used. Before cyclic voltammetry, working electrode was activated by cathodic polarization at -0.542 V vs SCE for 7200 seconds [52]. After pre-activation step, working electrode was scanned for 120 cycles between -0.242 and 1.2V at a scan rate of 100mV/s and the last cycle was performed in same potential range at a scan rate of 40 mV/s. Chronoamperometric analysis were done at 0.6V vs RHE for 600 seconds and the time

dependent current profiles were recorded. Chronopotentiometric analysis were done at 0.5 mA for 600 seconds and the time dependent potential profiles were recorded. All the electrochemical experiments (cyclic voltammetry, chronoamperometry, chronopotentiometry) were also carried out in a base electrolyte, 0.5M H₂SO₄ for the background subtraction (correction) of experiments performed in 0.5M H₂SO₄ + 0.5M C₂H₅OH electrolyte. All the home-made catalysts were compared with commercial PtRu/C (%20 Pt, %10Ru) electrocatalyst (Electrochem Inc.).

2.4. Fuel Cell Tests

Before fuel cell tests, membrane electrode assemblies (MEA) were prepared by hot press technique [53]. The anode electrode consisted of a thin carbon paper (Quintech Inc.) of ~100 microns which was painted with 12 wt% Nafion and 88 wt% PtRu/C (20wt % Pt, %10Ru, (Electrochem)) or home-made electro-catalyst ink. The cathode electrode consisted of a thin (134 microns) teflonized (20 wt%) carbon paper upon which was painted with 15 wt% Nafion + Pt black catalyst ink. The electrodes were painted until desired catalyst loading (~4mg/cm²) was achieved. The electrodes were placed on either side of a pre-treated N117, nafion membrane. The pre-treatment procedure involved boiling the membrane for 1hr period in a solution of deionized water and 0.5M H₂SO₄. The electrodes were hot pressed at 130°C, 400 psi for 5 min. After the preparation of membrane electrode assembly, it was set into fuel cell test station that consists of graphite blocks and pneumatic system (Greenlight TP5 Pneumatic fuel cell system); the air pressure on the graphite blocks was set to be 60 psia. MEA was conditioned for 24 hours by passing distilled water through fuel cell system at 80°C to hydrate polymer membrane. After conditioning the MEA, ambient air was fed to the cathode compartment by compressor, airflow rate was controlled by flowmeter and 1M ethanol was fed to the anode compartment by a peristaltic pump controlled by a liquid flow controller. The fuel cell temperature at 40°C, 60°C and 80°C was controlled by PID controller (Digisense). Fuel cell polarization curves were obtained by TDI Power Electronic Load unit.

3. RESULTS AND DISCUSSION

3.1 ICP-OES

Table 2. Metallic weight percentages of reduced catalysts

Reduced 400°C at	Ni%	Pt%	Fe%	Ce%	Pd%
Pt/NiCeO _x ^a	29.8±0.2	14.1±0.1		29.3±0.3	
Ni/PtCeO _x ^a	12.9±0.1	20.2±0.3		40.9±0.1	
Fe/PtCeO _x ^a		19.7±0.2	17.0±0.1	40.8±0.5	
Pt/FeCeO _x ^a		11.6±0.1	34.1±0.2	27.1±0.2	
Pt/PdCeO _x ^a		8.34±0.08		32.8±0.3	38.8±0.2
Pd/PtCeO _x ^a		25±0.2		40.2±0.2	5±0.09

^aCatalyst: A/BCeO_x, A: metal loaded on the surface, B: Metal added during hydrothermal synthesis, x: oxygen content in the support material.

In order to determine the bulk composition of electrocatalysts after H₂ reduction, ICP-OES analysis were done. In Table 2 below, metallic weight percentages of catalysts can be seen.

As a result of ICP analysis, it was seen that metal loadings on the surface are close to 10 wt % ranging between 5% and 17%. As mentioned before, targeted surface metal loading was 10%. Cerium loadings are between 27.1% and 40.9 wt% and Pt loading in the support phase (in BCeO_x) was between 19.7% and 25 wt%. The weight % of other transition metals in the support range between 29.8 and 38.8.

3.2 X-Ray Photoelectron Spectroscopy

It is known that XPS analysis is surface sensitive so weight percentage distribution shown below in Table 3 is valid for about 3-10 nm depth. After XPS analysis, it was also possible to compare surface elemental distribution with ICP (bulk) analysis. It was very crucial to see the difference between bulk and surface metal distributions since these distributions determine the effect of surface metals on the ethanol electro-oxidation rate (Table 4).

Table 3. Weight and molar percentages of reduced catalysts by XPS

Reduced 400°C at	Ni%		Pt%		Fe%		Pd%		O%		Ce%	
	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%	At.%	Wt.%
Pt/NiCeO _x	22	32.66	4.3	21.22	-	-	-	-	68.4	27.68	5.2	18.43
Ni/PtCeO _x	9.1	9.81	8.5	30.44	-	-	-	-	66.8	19.62	15.6	40.13
Fe/PtCeO _x	-	-	5.1	18.26	31.9	32.70	-	-	49.6	14.57	13.4	34.47
Pt/FeCeO _x	-	-	4.4	16.50	33.6	36.06	-	-	50.1	15.40	11.9	32.04
Pt/PdCeO _x	-	-	2.1	9.29	-	-	16.1	38.84	73.8	26.77	7.9	25.1
Pd/PtCeO _x	-	-	8	31.56	-	-	1.12	2.41	76.2	24.66	14.6	41.37

After XPS analysis, it was seen in Table 3 that the oxygen contents of catalysts are between 14.57 and 27.68 wt %. Therefore if they are arranged from highest to lowest, it would be Pt/NiCeO_x> Pt/PdCeO_x>Pd/PtCeO_x> Ni/PtCeO_x> Pt/FeCeO_x> Fe/PtCeO_x. Low oxygen content in Fe/PtCeO_x may be the sign of high amount of oxygen vacancies in ceria composite support which are known to be active sites for adsorption and removal of surface poisoning species [12, 14, and 15].

Table 4. Comparison of XPS with ICP-OES analysis

Reduced T=400°C	Ni%		Pt%		Fe%		Ce%		Pd%	
	Surface ^b	Bulk	Surface ^b	Bulk	Surface ^b	Bulk	Surface ^b	Bulk	Surface ^b	Bulk
Pt/NiCeO _x	45.17	29.8±0.2	29.34	14.1±0.1	0.00		25.49	29.3±0.3		
Ni/PtCeO _x	12.20	12.9±0.1	37.87	20.2±0.3	0.00		49.93	40.9±0.1		
Fe/PtCeO _x	0.00		21.38	19.7±0.2	38.28	17.0±0.1	40.35	40.8±0.5		
Pt/FeCeO _x	0.00		19.50	11.6±0.1	42.62	34.1±0.2	37.88	27.1±0.2		
Pt/PdCeO _x			12.68	8.34±0.08			34.27	32.8±0.3	53.05	38.8±0.2
Pd/PtCeO _x			41.89	25±0.2			54.91	40.2±0.2	3.20	5±0.09

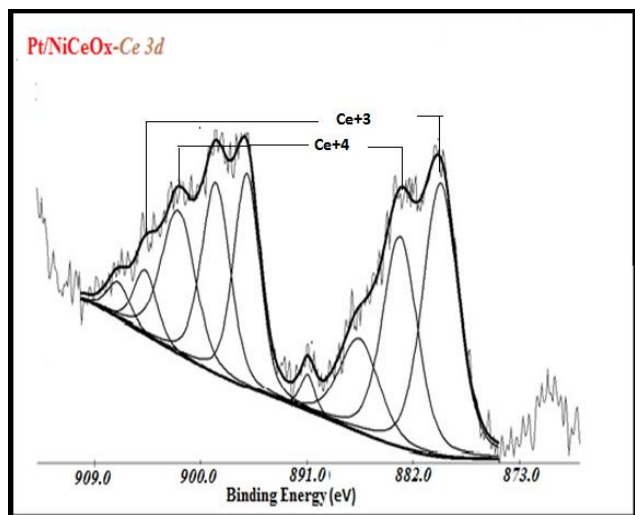
^bIn order to compare XPS with ICP analysis, oxygen content was removed from elemental analysis of XPS and the weight % distribution was recalculated.

In Table 4, surface segregation of metals can be clearly seen and can be investigated in the case of different bulk and surface catalyst phase combinations. Therefore according to Table 4, surface Pt and Ni was higher compared to bulk phase in Pt/NiCeO_x, in the case of Ni/PtCeO_x, only surface Pt was higher than bulk phase. In Fe/PtCeO_x, surface Fe was almost two folds higher compared bulk phase. In Pt/FeCeO_x, both surface Pt and Fe had higher percentages compared to bulk. Also in Pt/PdCeO_x, Pt and Pd was higher on the surface but surface Pd was incomparably higher than surface Pt.

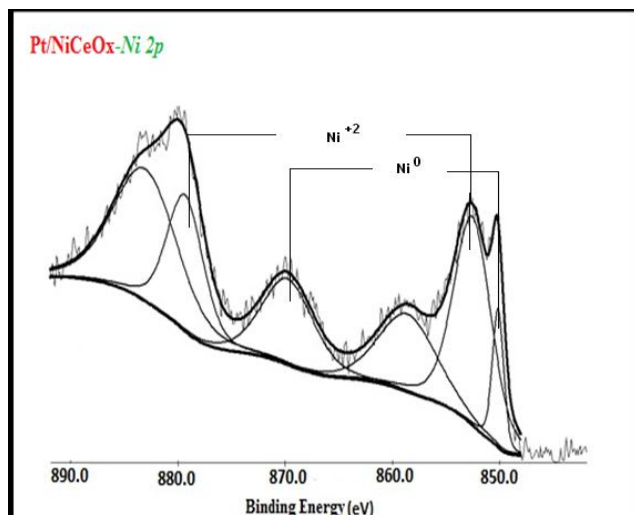
It is widely known that, heat of sublimation has an important effect on surface segregation. In the case of Pt/PdCeO_x, although Pd is loaded in the support phase, since Pd has much lower sublimation heat (89.9 kcal/mol [54]) than Pt (135.04 kcal/mol [55]), it has higher tendency to segregate to the surface and compete with Pt. Or in the case of Fe/PtCeO_x, although Pt is loaded at a higher weight percentage in the support, since the sublimation heat of Pt is higher than Fe (96.7 kcal/mol [56]), we can not expect Pt to segregate to the surface as strong as Fe.

Table 5. Comparison of XPS with ICP-OES analysis

	Pt/NiCeO _x	Ni/PtCeO _x	Fe/PtCeO _x	Pt/FeCeO _x	Pt/PdCeO _x	Pd/PtCeO _x
Degree of surface segregation	Surface segregation of both	Surface Segregation of Pt	Surface segregation of Pt and strong surface segregation of Fe	Surface segregation of Pt and surface segregation of Fe	Surface segregation of Pt and strong surface segregation of Pd	Surface segregation of Pt
Most probable surface dominant	Pt, Ni, Ce oxides	Pt, Ni, Ce oxides	Pt, Fe, Ce oxides	Pt, Fe, Ce oxides	Pt, Pd, Ce oxides	Pt, Ce oxides
O to Ce atomic ratio	13.15	4.3	3.7	4.2	9.3	5.2
Order of surface metals	Ni>Pt>Ce	Ce>Pt>Ni	Ce>Fe>Pt	Fe>Ce>Pt	Pd>Ce>Pt	Ce>Pt>Pd



A



B

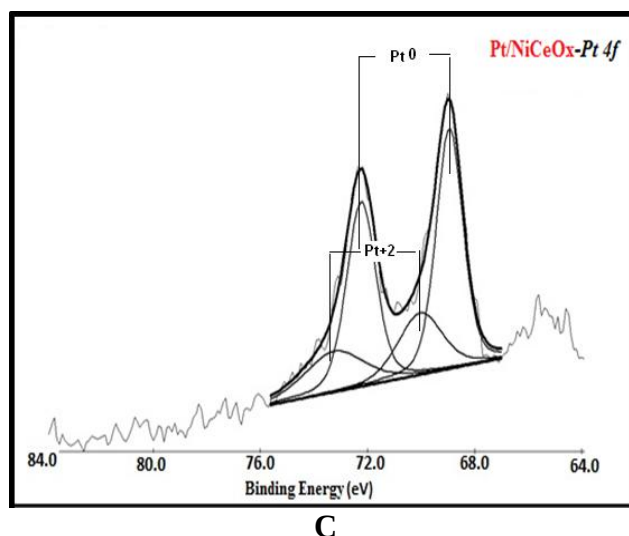


Figure 1. Analysis of XPS spectra of Pt/NiCeO_x. **A** Ce 3d. **B** Ni 2p. **C** Pt 4f.

By the use of atomic % in Table 3 and 4, the oxygen to cerium atomic ratio and the degree of surface segregation can also be determined. These parameters that are combined in Table 5, helped us to understand the source of oxygen on the surface other than stoichiometric or non-stoichiometric ceria, and to see the surface transition metals that are involved in ethanol electro-oxidation.

It is very clear from Table 5 that oxygen to cerium atomic ratio increases when platinum in the support phase is exchanged by an other transition metal. This may be both due to surface oxygen and due to the formation of different oxide phase of iron and nickel (other than ceria) in the support and at the surface. Oxygen to cerium atomic ratio and the order of surface metals indicate that in the ethanol oxidation mechanism, mostly mixed cerium and Ni, Fe, Pd and even Pt oxides can be involved with metallic Pd and Pt.

For the deconvolution of orbital peaks in XPS spectra, XPSPEAK41 software was used. Table 1 was used for the determination of binding energy shifts of Ce 3d, Pt 4f, Ni 2p and Fe 2p orbital peaks and ionic structures. Figure 1A shows deconvoluted XPS spectra of Ce 3d core level region, binding energies of Ce⁺⁴ and Ce⁺³ can be seen together with the satellite peaks. From the deconvoluted spectra, a mixed ionic phase could be seen. Deconvoluted peak intensities indicate that Ce⁺³/Ce⁺⁴ ratio is 1.3 approximately. In Figure 1B, Ni 2p spectra shows high Ni⁺²/Ni⁰ ratio. Presence of Ni⁺² in the support phase is most probably due to the formation of NiO. In contrast to Ni 2p, doublets in Pt 4f spectra indicates that Pt⁰ dominates over Pt⁺² with a Pt⁰/Pt⁺² ratio of 2.4.

Similar to Pt/NiCeO_x, Figure 2A also indicates a mixed ionic phase with a Ce⁺³/Ce⁺⁴ ratio of 1.6. Pt 4f spectra in Figure 2B shows no ionic Pt. In addition, very high Ni⁺²/Ni⁰ ratio (~ 5.4) can be seen in Ni 2p partial scan of impregnated surface Ni.

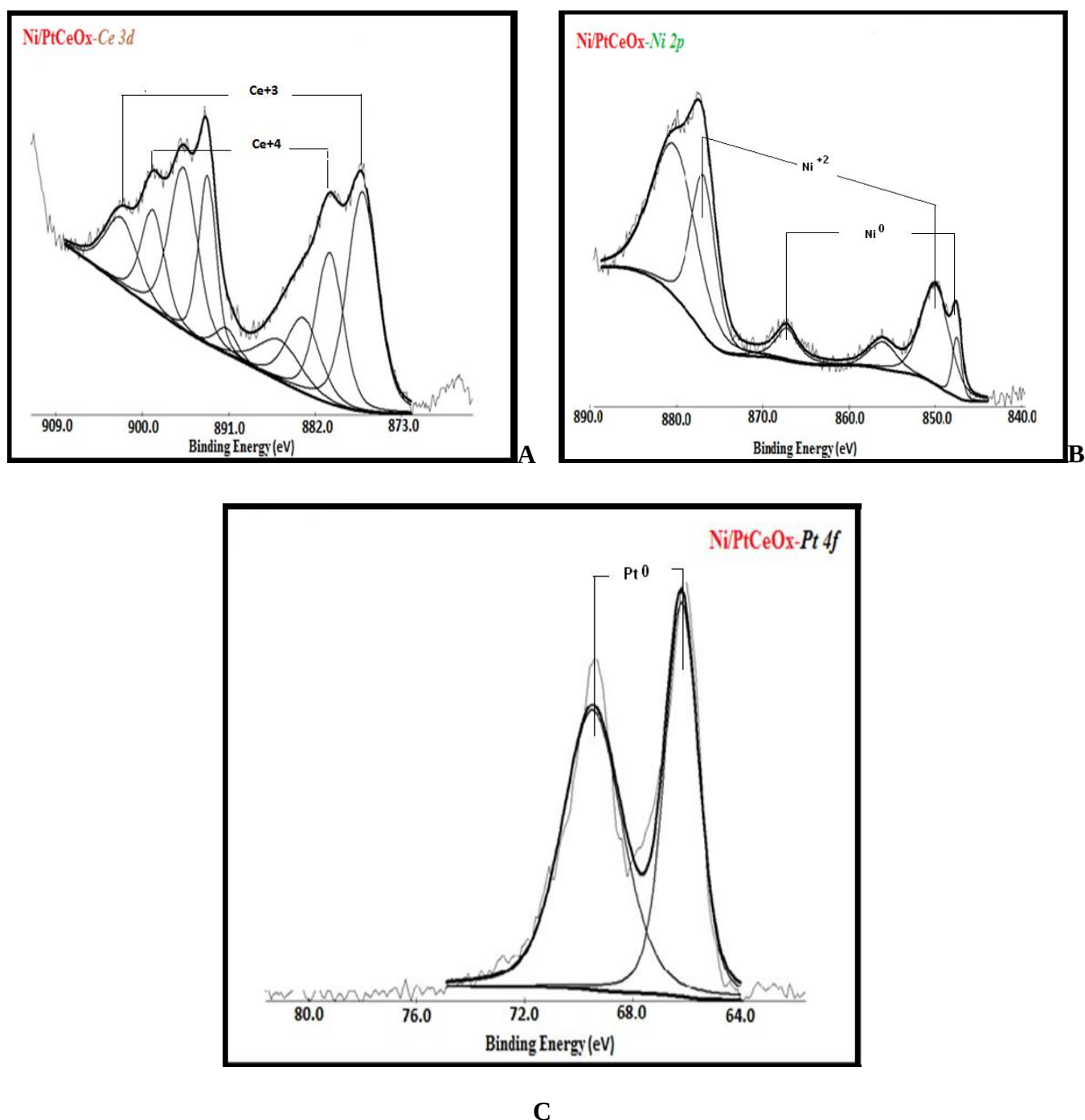


Figure 2. Analysis of XPS spectra of Ni/PtCeOx. **A** Ce 3d. **B** Ni 2p. **C** Pt 4f.

Doublet at 714.8 and 718.9 eV in Figure 3B corresponds to $\text{Fe}^{+3} 2p^{3/2}-2p^{1/2}$. In addition, binding energy of $\text{Fe} 2p^{3/2}$ at 706 eV shows evolution of metallic iron. In Figure 3C, Pt 4f orbital structure has similar behavior to Ni/PtCeOx (Figure 2C) with a pure Pt^0 state. And Ce3d spectra in Figure 3A exhibits a mixed ionic phase where the $\text{Ce}^{+3}/\text{Ce}^{+4}$ ratio is very close to 1.

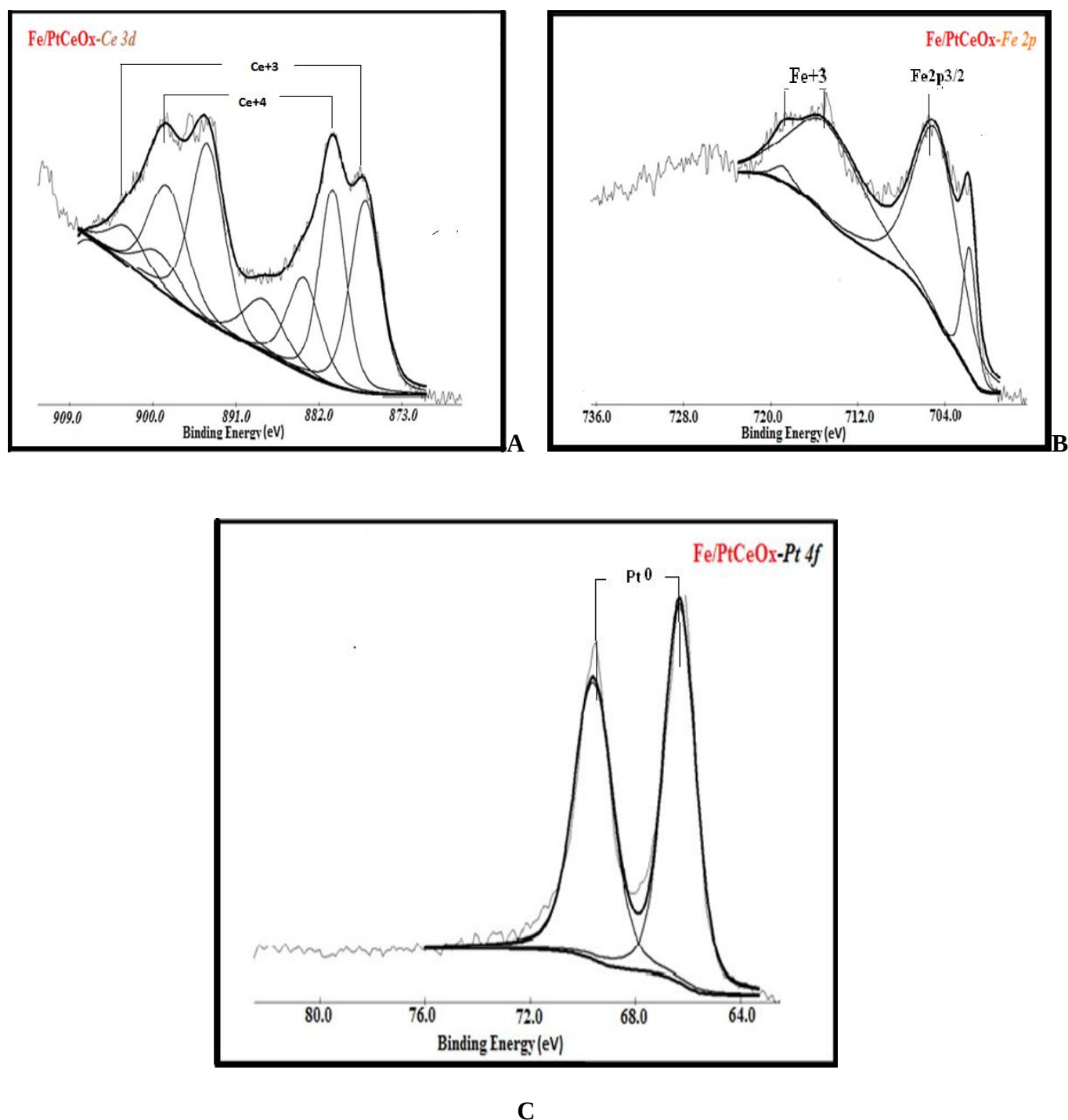


Figure 3. Analysis of XPS spectra of Fe/PtCeOx. **A** Ce 3d. **B** Fe 2p. **C** Pt 4f.

In Figure 4, in contrast to electro-catalysts mentioned previously, Ce3d spectra has higher peak intensity at 881.45 eV which is caused by high amount of CeO₂. Therefore Ce³⁺/Ce⁴⁺ ratio is lower than one (~0.8). Doublet at 718.9 and 713.7 eV and the single peak at 706 eV in Figure 4 is similar to Fe 2p spectra in Fe/PtCeOx which also indicates an iron oxide phase. Pt 4f core level region exhibits a doublet at 67.3 and 70.6 eV which correspond to Pt⁰.

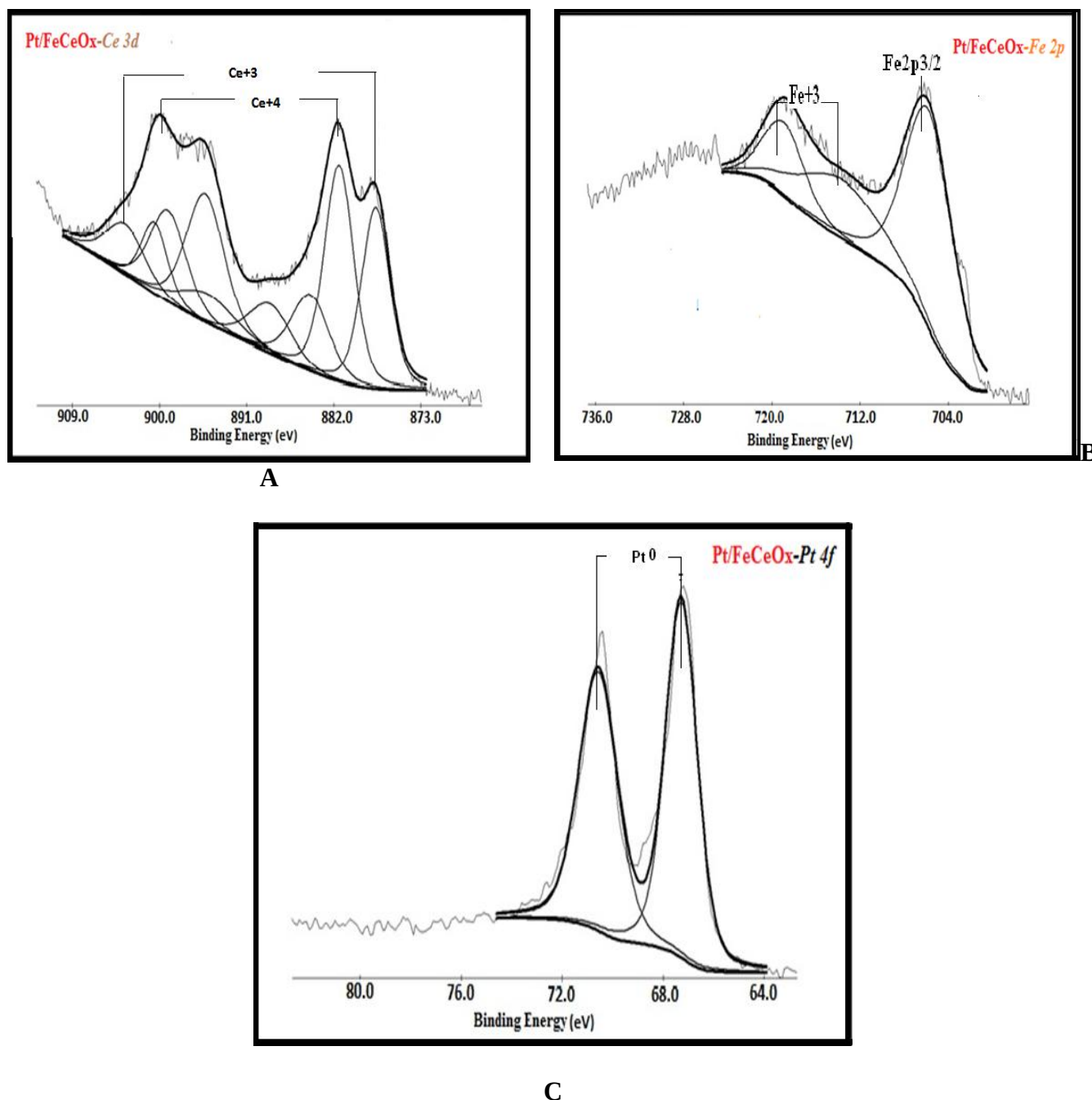


Figure 4. Analysis of XPS spectra of Pt/FeCeOx. **A** Ce 3d. **B** Fe 2p. **C** Pt 4f.

Similar to Fe doped ceria in Figure 5, doublets detected at 881.5, 901 eV and 876, 904 eV are due to a mixed oxide phase of ceria and the $\text{Ce}^{+3}/\text{Ce}^{+4}$ ratio is again less than one (~ 0.8). Pt 4f spectra with two doublets at 64.68 eV and 66.70 eV can be interpreted as the formation of $\text{Pt}^{+2}/\text{Pt}^0$ mixed ionic phase. The $\text{Pt}^{+2}/\text{Pt}^0$ ratio is 0.6. Pd 3d spectra only shows the existence of Pd^0 at 328 and 334 eV.

In Figure 6, higher intensity of Ce^{+4} compared to Ce^{+3} doublet is also an indication of less Ce_2O_3 and lower oxygen vacancy ($\text{Ce}^{+3}/\text{Ce}^{+4} \approx 0.4$). One doublet at 70 and 66 eV in Pt 4f spectra and

deconvoluted region between 336 and 334 eV in Pd 3d spectra are due to pure Pt^0 and $\text{Pd}^0/\text{Pd}^{+2}$ mixed ionic phase.

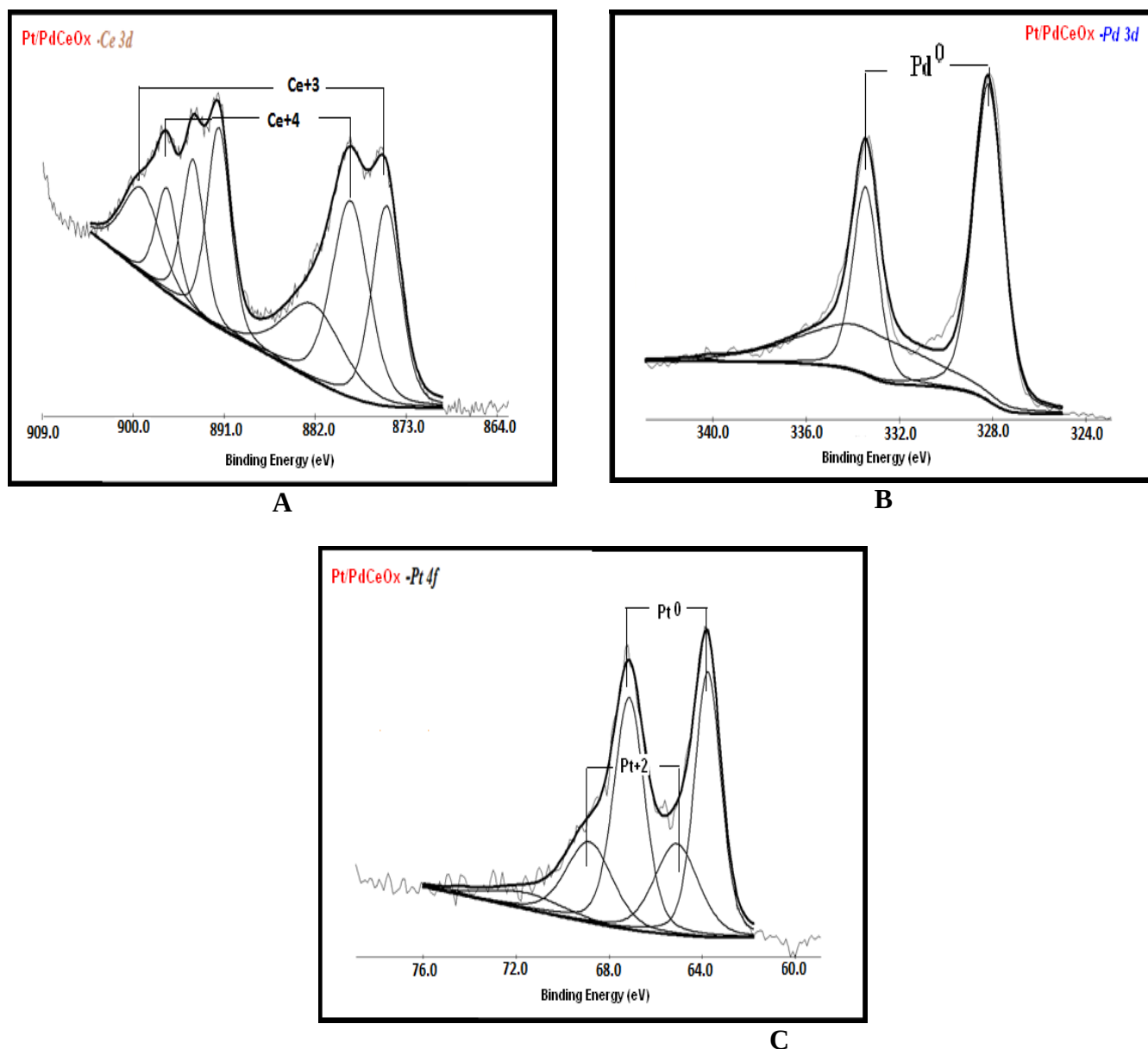


Figure 5. Analysis of XPS spectra of Pt/PdCeOx. **A** Ce 3d. **B** Pd 3d. **C** Pt 4f.

3.3 X-Ray Diffraction (XRD)

In Figure 7, XRD pattern of Pt/FeCeOx and Pt/PdCeOx show characteristic crystalline peaks of Fe_3O_4 , Fe, Pt, Pd and CeO_2 . Intensity of Fe crystalline peaks in Pt/FeCeOx are higher compared to Fe_3O_4 which was due to hydrogen reduction. Oxide phase in Pt/FeCeOx is most probably composed of $\text{Fe}_3\text{O}_4 + \text{CeO}_2$ in addition to metallic Pt and Fe. Pt (111) crystalline peak at 40° was very low for Fe/PtCeOx. On the other hand, CeO_2 and Fe crystalline peaks are higher compared to Pt peaks. The

behavior of Ni/PtCeO_x was similar to Fe/PtCeO_x and Pd/PtCeO_x. In contrast to Pt, CeO₂ peaks were again much higher in Ni/PtCeO_x. This results show that Pt most probably diffused into ceria matrix in Ni/PtCeO_x, Fe/PtCeO_x and Pd/PtCeO_x. Ni, Pt and NiCeO₂ crystal peaks can be seen on Pt/NiCeO_x.

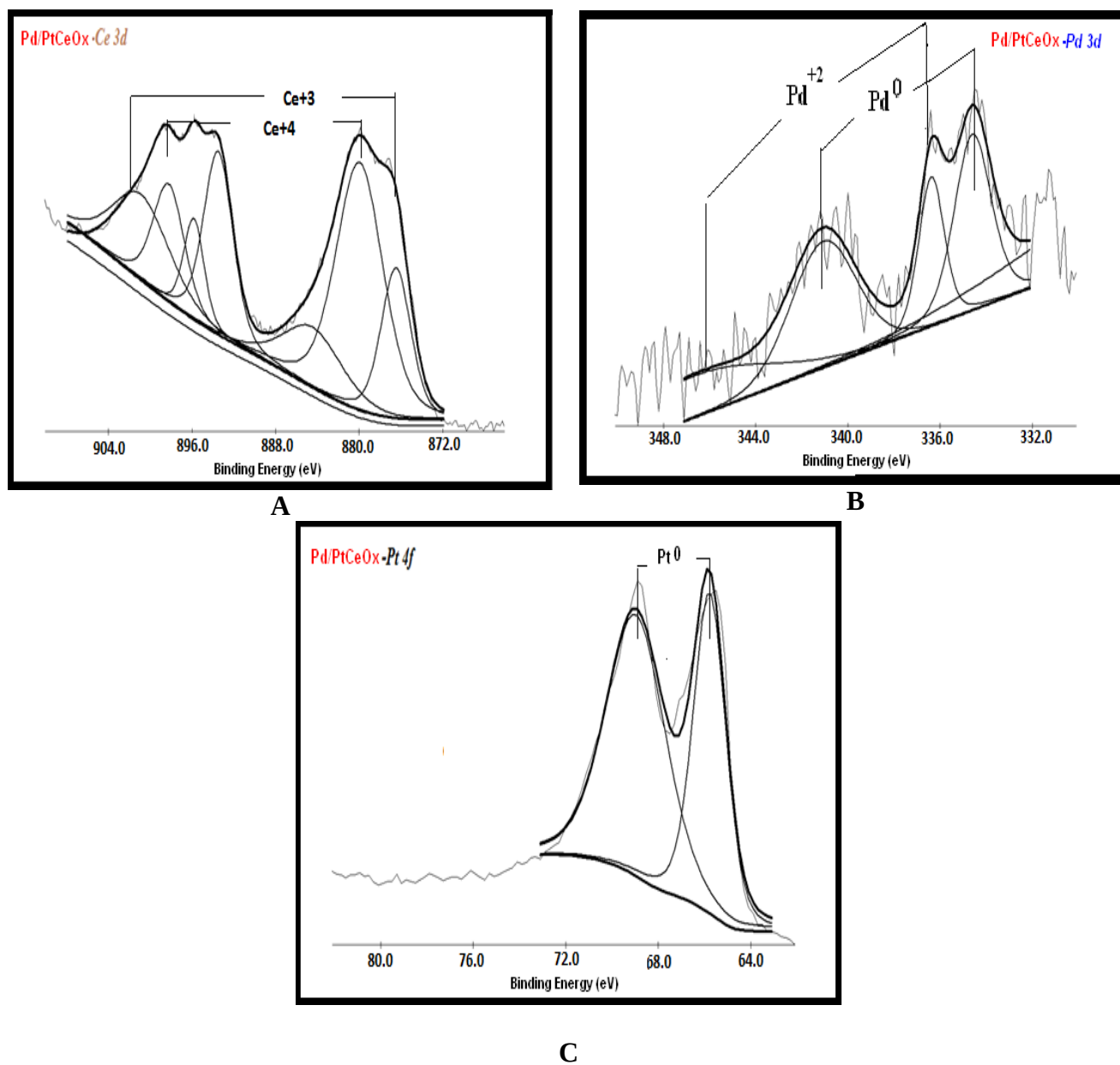


Figure 6. Analysis of XPS spectra of Pd/PtCeO_x. **A** Ce 3d. **B** Pd 3d. **C** Pt 4f.

Like in the case of PtCeO₂, it seems that it was also possible to incorporate Ni and Pd into the CeO₂ matrix. XPS results support the existence of Fe₃O₄ by the doublet in Figure 3B, 4B and also support the existence Pt⁰ and Pd⁰ by Pt 4f and Pd 3d core level regions in Figure 2C, 3C, 4C, 5B, and 6C.

3.4 Transmission Electron Microscopy (TEM)

In order to determine the geometric structure and the particle size, support phases were analyzed by TEM. In Figure 8A, NiCeOx support phase has approximately 50 nm particle size and both hexagonal nano platelets can be seen. These hexagonal multi-facet nanocrystalline structures are most probably related to NiO [57]. In Figure 8B and 8D, unlike NiCeOx, 50 nm particular structures were seen in PtCeOx and PdCeOx phases. In Figure 8C, FeCeOx exhibit 50 nm particular structures on micron-size rods. According to the literature, these rod like and particular structures are supposed to be Fe₃O₄ and ceria respectively [58].

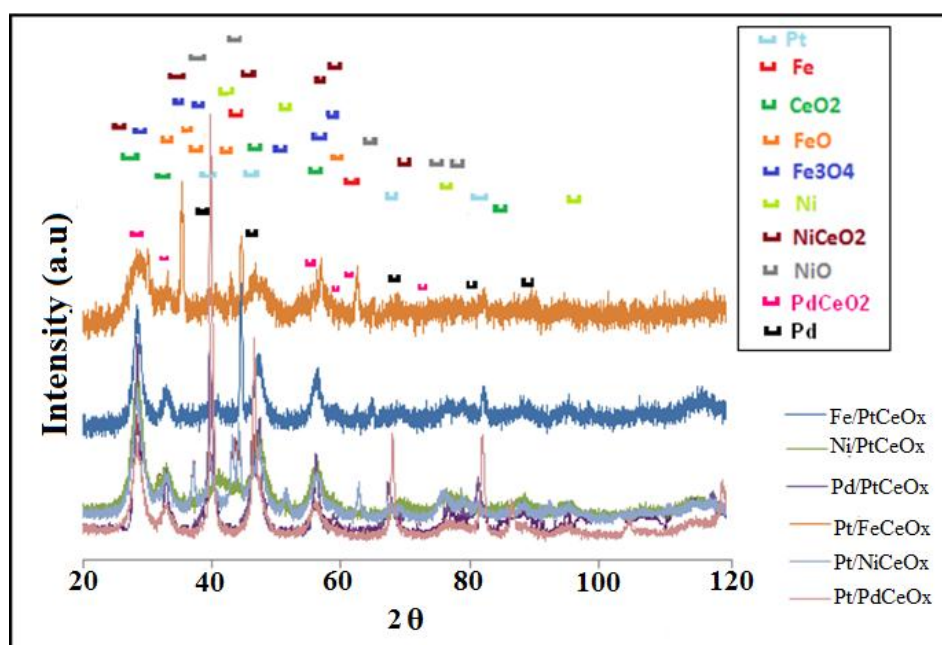
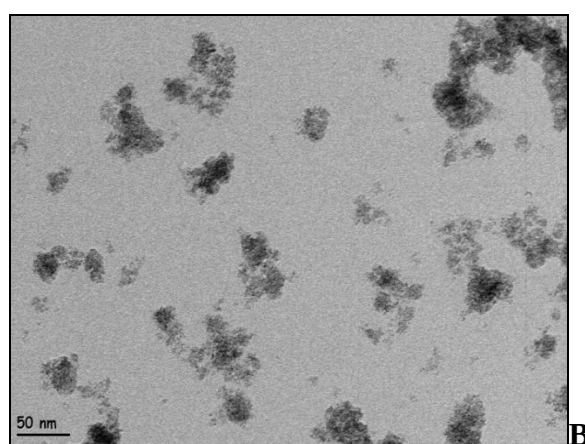
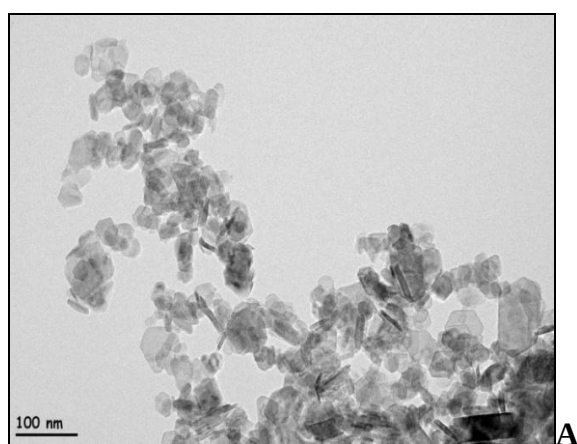


Figure 7. XRD patterns of home-made electrocatalysts prepared by impregnation-hydrothermal method.



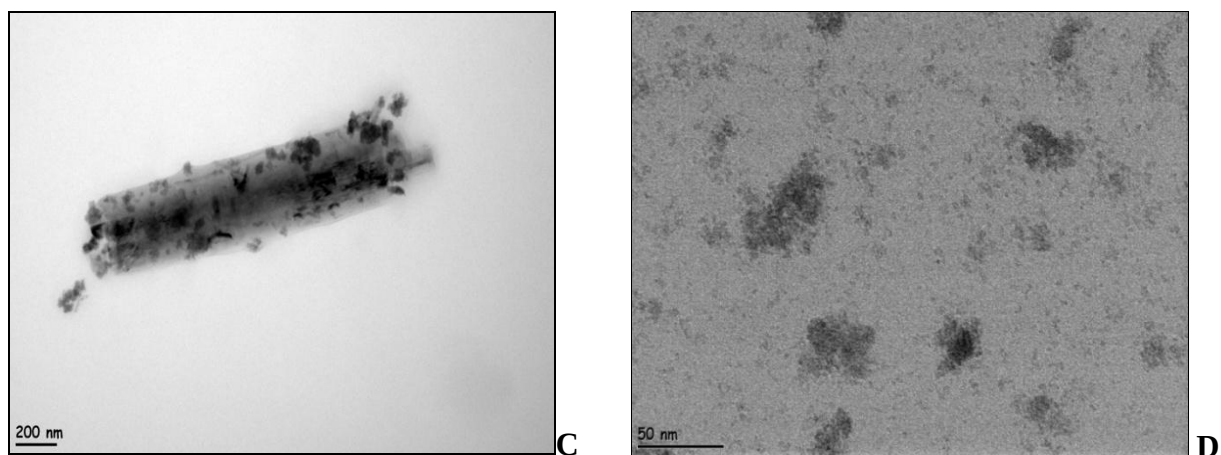
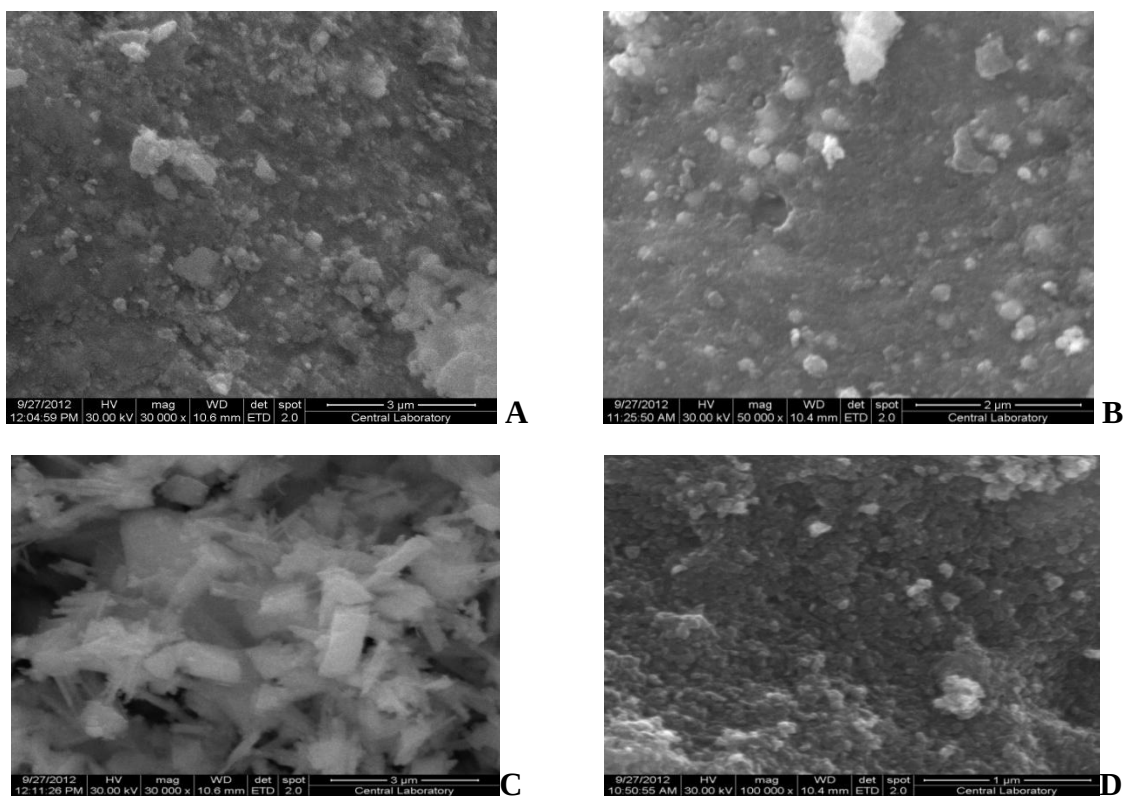


Figure 8. TEM images of **A** NiCeOx. **B** PtCeOx. **C** FeCeOx. **D** PdCeOx

3.5 Scanning Electron Microscopy (SEM)

SEM images of four home-made catalysts in Figure 9 show that Fe/PtCeOx and Pd/PtCeOx has somewhat non-uniform particle size ranging from 100 nm to 1 μ m (Figure 9A,E).



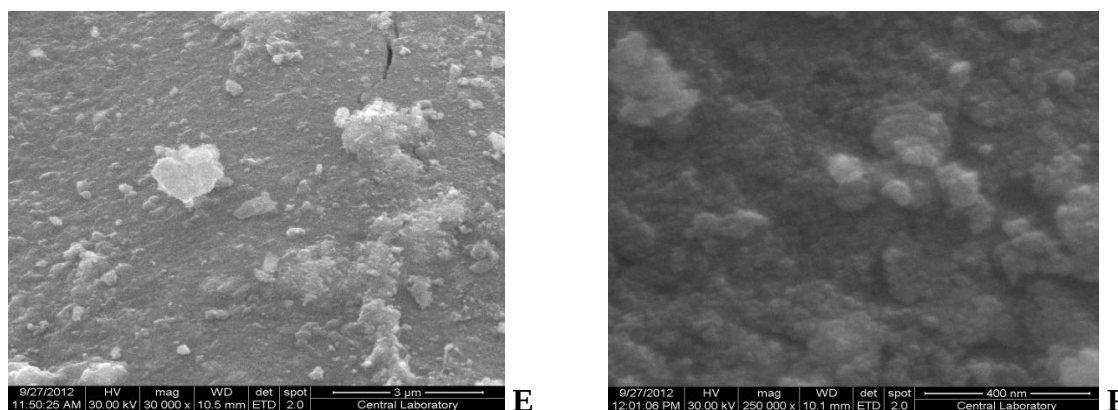


Figure 9. SEM analysis of home-made electrocatalysts. **A** Fe/PtCeOx. **B** Ni/PtCeOx. **C** Pt/FeCeOx. **D** Pt/NiCeOx. **E** Pd/PtCeOx. **F** Pt/PdCeOx.

On the other hand, Ni/PtCeOx (Figure 9B) has more uniform structure approximately with 20-50 nm particle size. Micron size, nano-needle and rod like structures can be seen on Pt/FeCeOx (Figure 9C). As we mentioned before, these nano-needle or rod like structures correspond to iron oxide phase. Pt/NiCeOx and Pt/PdCeOx (Figure 9D,F) exhibit similarly uniform structure approximately with in 100 nm particle size.

3.6 Cyclic Voltammetry

In Figure 10, comparison of home-made electrocatalysts with commercial PtRu /C ((20%Pt10%Ru), Electrochem Inc.) can be seen. Cyclic voltammograms exhibit typical irreversible ethanol electro-oxidation peaks. During cyclic voltammetry, electrocatalysts which have higher peak currents compared to PtRu/C can be determined. When electrocatalysts were arranged in the order of peak currents, it was seen that: Fe/PtCeOx > Pt/PdCeOx > PtRu/C. Forward peaks close to 0.8V and backward peaks close to 0.4 V most probably indicate direct ethanol electro-oxidation to CO₂ and oxidation of surface carbonaceous species. Therefore the high ratio of forward peak to backward peak on both Fe/PtCeOx and Pt/PdCeOx means higher electrochemical performance and high tolerance to poisoning [14,15,59,60]. The two oxidation peaks at ~0.4 and ~0.8V which are very significant for Fe/PtCeOx may be due to the oxygenated species adsorbed on oxygen vacancy sites of PtCeOx composite support and Fe oxides (which were observed by XRD, XPS and TEM measurements). These promoters facilitate electro-oxidation of ethanol through bifunctional mechanism [26,30,31,61]. Although theoretically, ethanol electro-oxidation release high number of protons (12H⁺), strongly adsorbed C₂ surface products formed during decomposition, dramatically drop electro-catalytic performance. Therefore on Fe/PtCeOx and Pt/PdCeOx, adsorbed species can be removed at higher rates due to the bifunctional effect mentioned above [62].

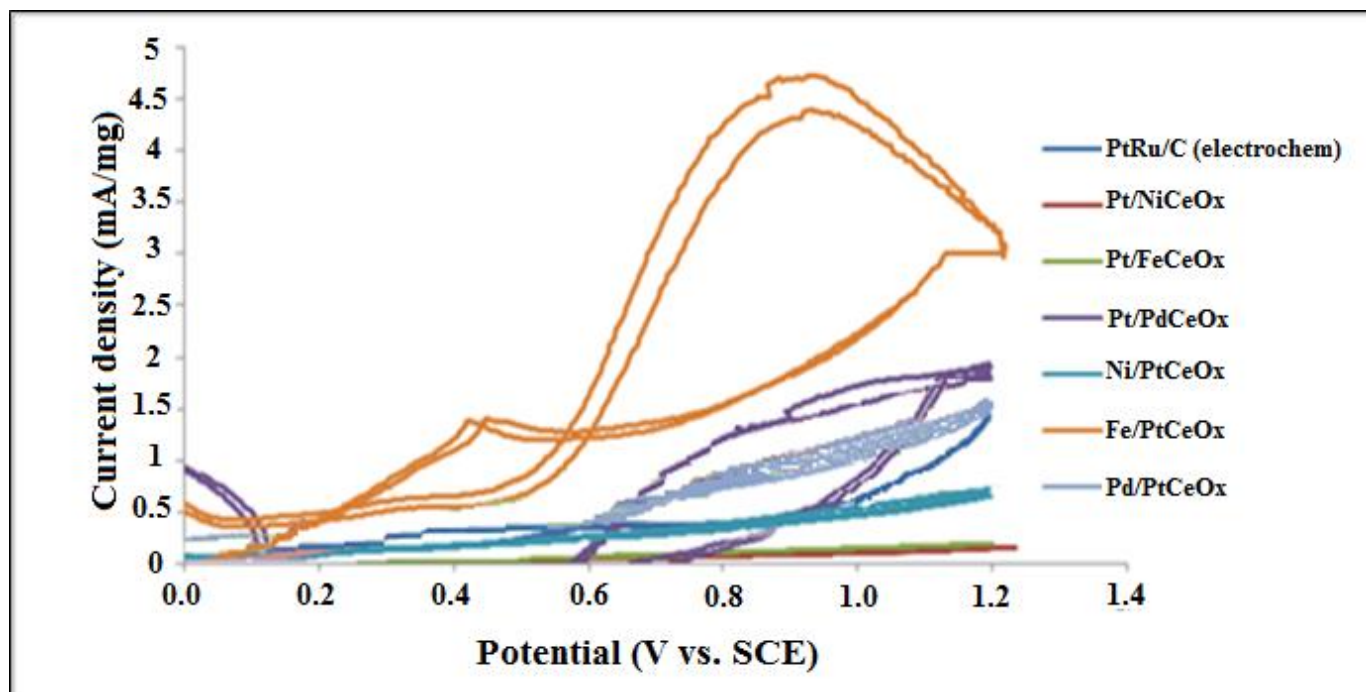


Figure 10. Cyclic voltammograms of home-made catalysts. Scan rate: 40mV/sec. Electrolyte: 0.5M H_2SO_4 + 0.5M $\text{C}_2\text{H}_5\text{OH}$. $T=25^\circ\text{C}$.

3.7 Chronoamperometry

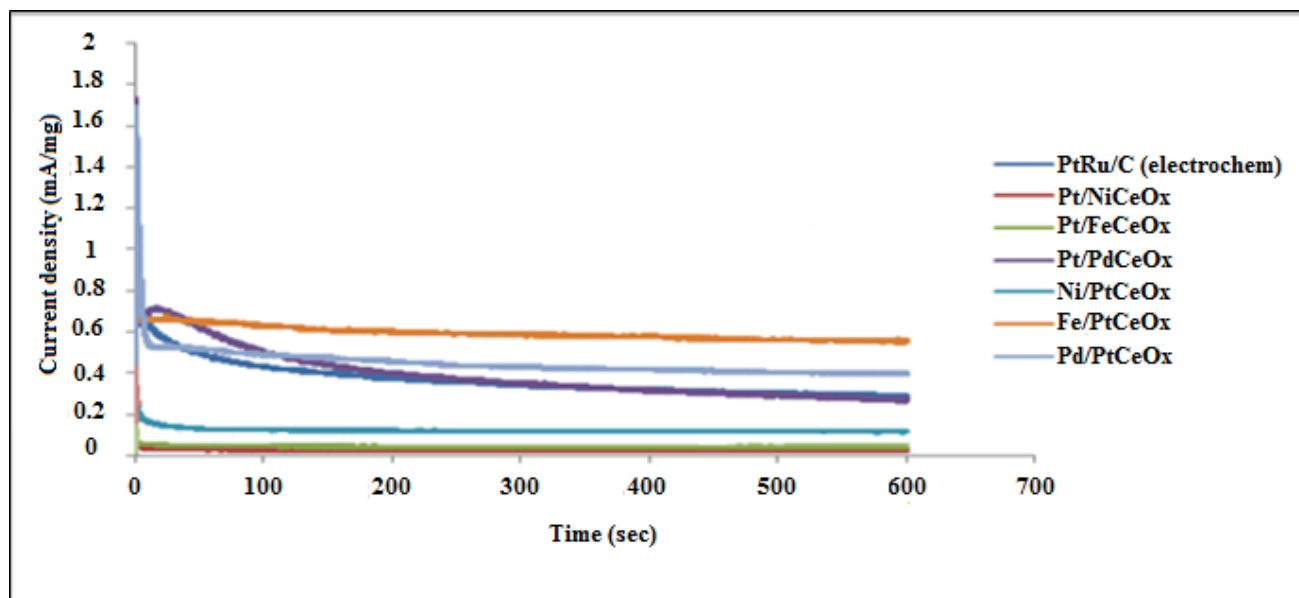


Figure 11. Chronoamperometric analysis of home-made catalysts. Potential: 0.6V vs. RHE. Electrolyte: 0.5M H_2SO_4 + 0.5M $\text{C}_2\text{H}_5\text{OH}$. $T=25^\circ\text{C}$

In general, the stability of the electrocatalyst and tolerance to poisoning species can be determined by chronoamperometric tests (carried out at a specific oxidation potential). During ethanol electro-oxidation (or decomposition), both at low and high potentials, adsorbed CO or C_2 species

accumulate and poison catalytically active sites. This process can be observed in Figure 11 by current drop after double layer charging (sudden drop) during 200sec. However as the oxidation process proceeds, the rate of current drop decreases because of competing reactions of adsorption(poisoning) and oxidative removal poisoning species by bifunctional mechanism that leaves available sites for oxidation. And finally current reaches a steady state. The steady state value of current indicates relative magnitude of oxidative removal rate to poisoning rate and the degree of catalyst stability[62,63].

In Figure 11, at 0.6 V, it was seen that the current profile of Fe/PtCeOx and Ni/PtCeOx reach steady state in 10 minutes. The highest steady state current density was achieved for Fe/PtCeOx. Magnitudes of steady state current densities can be arranged in order as: Fe/PtCeOx>Pd/PtCeOx>PtRu/C $\approx$ Pt/PdCeOx. Therefore, the order of steady state current densities shows that Fe/PtCeOx is the most stable and the most efficient anti-poisoning catalyst in this oxidation environment.

3.8 Chronopotentiometry

At an applied current of 0.5 mA, the change in the electrode potential and the steady state potentials gave important information about anodic polarization. Lower anodic polarization is a criteria for a good electrocatalyst performance. In Figure 11, the lowest anodic polarization was achieved for Fe/PtCeOx. If the steady state potentials are arranged in order, it is seen that: Fe/PtCeOx< Pt/PdCeOx<PtRu/C <Pd/PtCeOx. In Figure 11, it is seen that at constant applied current, potential increase with time. Because, in order to supply the applied current needed for oxidative removal of adsorbed species during ethanol oxidation, electrode potential should be increased (electrode should be polarized). Therefore, the low steady state potential of Fe/PtCeOx means that lower polarization (or overpotential) is required at the same oxidative removal rate (current) and also means lower onset potentials for the formation of oxygenated species [62].

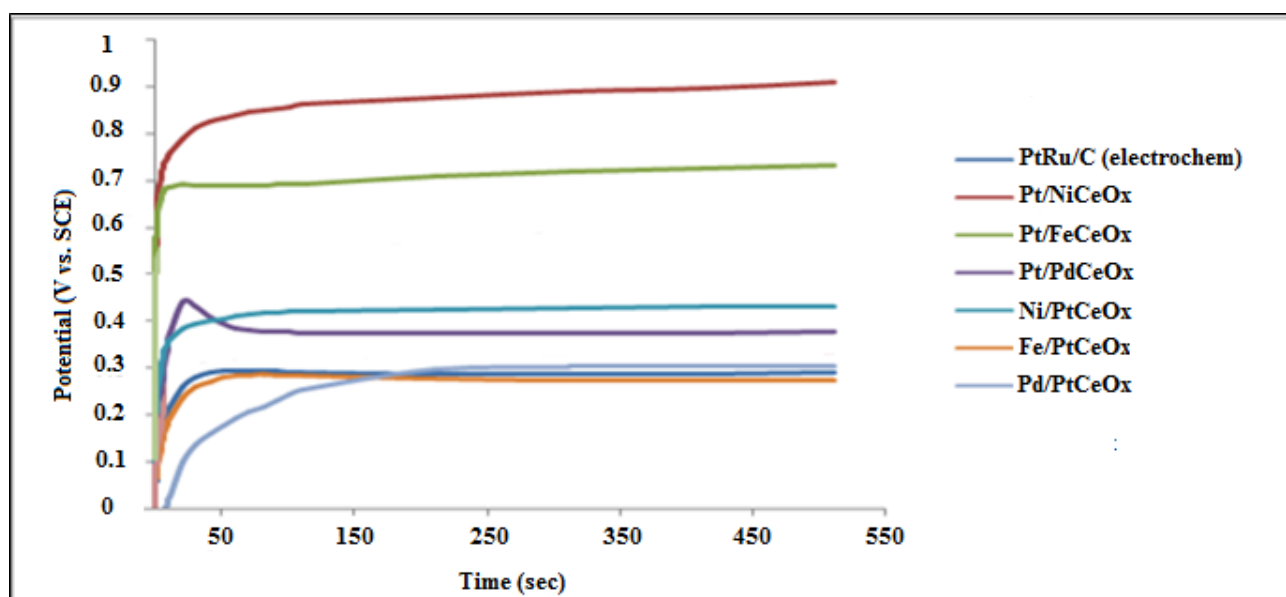


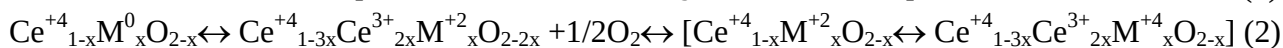
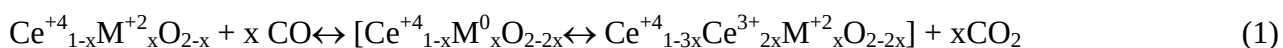
Figure 12. Chronopotentiometric analysis of home-made catalysts. Current: 0.5mA. Electrolyte: 0.5M H_2SO_4 + 0.5M $\text{C}_2\text{H}_5\text{OH}$. $T=25^\circ\text{C}$.

3.9. Fuel Cell Performance Tests

Fuel cell performance tests were carried out at three different temperatures (40, 60, and 80°C). As seen in Figure 13, highest current density (15mA/cm²) close to PtRu/C was obtained for Pt/PdCeOx. Despite lower current densities, at 80°C, the power density of Pt/PdCeOx (3.8mW/cm²) in Figure 15 was very close to the power density of PtRu/C at 60°C (4.5mW/cm²). Polarization curves clearly demonstrate that PtRu/C performance is more intensely affected by the fuel cell temperature. Although, power densities of home-made electrocatalysts are close to PtRu/C at 40°C, at higher temperatures the performance gap increased. This is due to the superior kinetic behaviour of PtRu/C. Since home made catalysts exhibit lower fuel cell performance than commercial PtRu/C, it was also decided to physically mix home-made and commercial catalysts (50:50 wt %) in a catalyst ink and to observe the boosting effect. Current and power densities shown in Figure 14 and 16 clearly show that home-made catalysts proved to have a boosting effect by physically mixing; in addition Ni/PtCeOx+PtRu/C, Pt/FeCeOx+PtRu/C and Pt/PdCeOx+PtRu/C catalyst mixtures can exceed the performance of PtRu/C.

The boosting effect of ceria based Ni/PtCeOx, Pt/FeCeOx and Pt/PdCeOx composite electrocatalysts observed in power and polarization curves can be related to different distinguishing physical and chemical properties: Comparison of surface, bulk compositions, order of surface metals and determination of oxygen to cerium atomic ratios show that surface dominance of ceria, Fe oxide and Pd is a major factor in high activities [64,65].

The existence of Fe₃O₄ and metallic palladium was identified clearly by XPS, XRD, SEM and TEM studies. All of these oxides and Pd is very well known by their superior oxygen transfer, corrosion inhibition, and CO or ethanol electro-oxidation activity. Secondly, from XRD and XPS studies, it was evident that Pd and Pt were incorporated into ceria structure and therefore may have changed the stability of ceria. It is very well known that [66] addition of Pt into ceria matrix dramatically change the redox behavior, make Ce⁺⁴ regenerative and conserve the oxide structure. The reversible redox mechanism during carbon monoxide can be shown by the following reactions:



In this mechanism M represents noble metal in the ceria structure. When surface poison CO interacts with lattice oxygen, electron transfer from transition metal to Ce⁺⁴ starts a reversible redox mechanism and increases oxygen vacancies which is why metal doped ceria is more active than pure ceria. When the boosting effect of Ni/PtCeOx, Pt/FeCeOx and Pt/PdCeOx on PtRu/C is considered, it is also the electron transfer from Pt or Pd to ceria that creates high oxygen vacancies for adsorption of ethanol decomposition products and bifunctional effect of Fe₂O₃ or NiO that can clean catalyst surface by removing decomposition products [26].

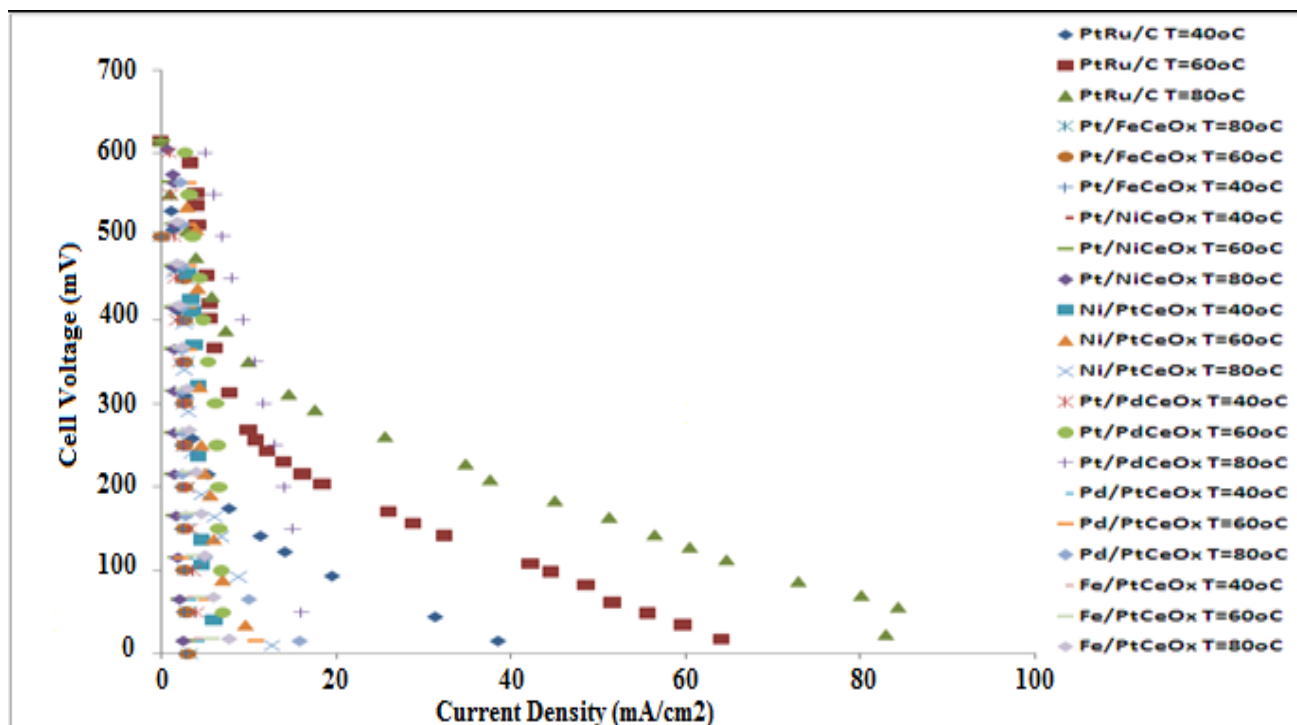


Figure 13. Full Cell polarization experiments: 1M ethanol flow rate:11ml/min, Dry air flow rate: 40ml/min. Fuel cell temperatures: 40,60,80°C.

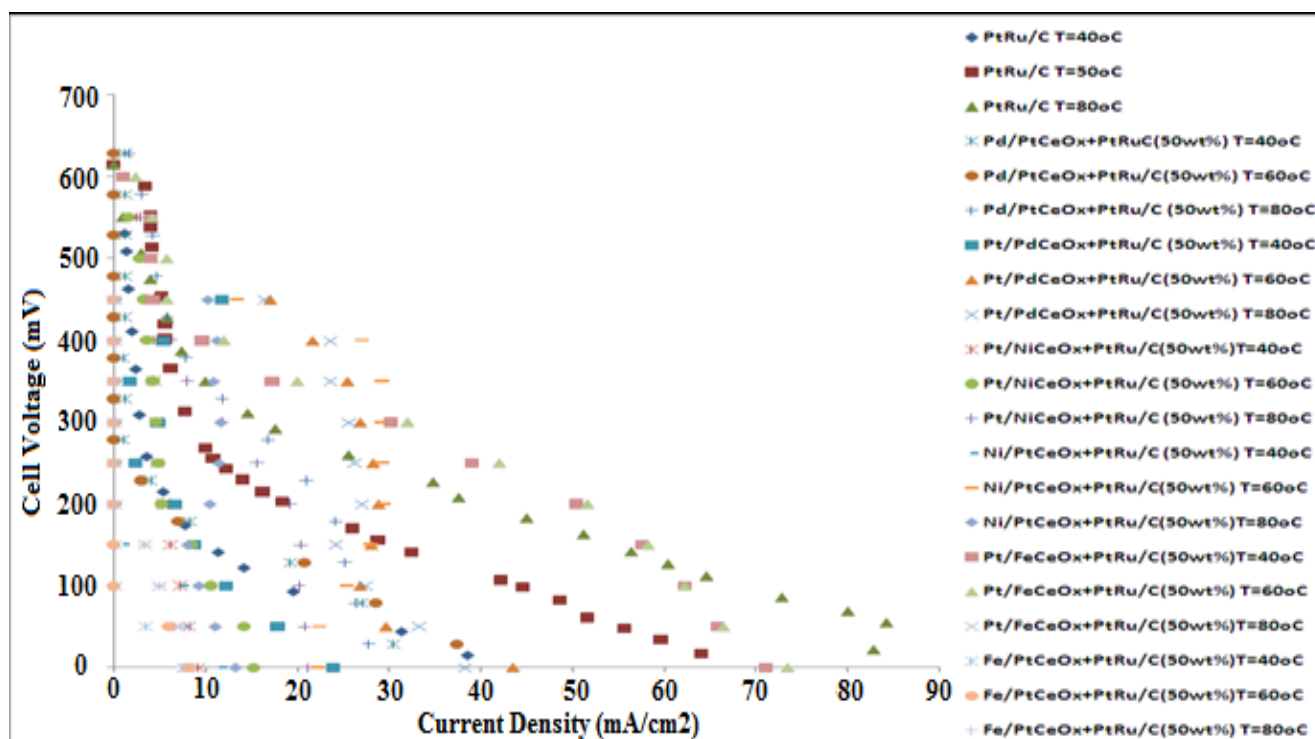


Figure 14. Full Cell polarization experiments: 1M ethanol flow rate:11ml/min, Dry air flow rate: 40ml/min. Fuel cell temperatures: 40,60,80°C. Comparison physically mixed catalysts with pure PtRu/C commercial catalyst.

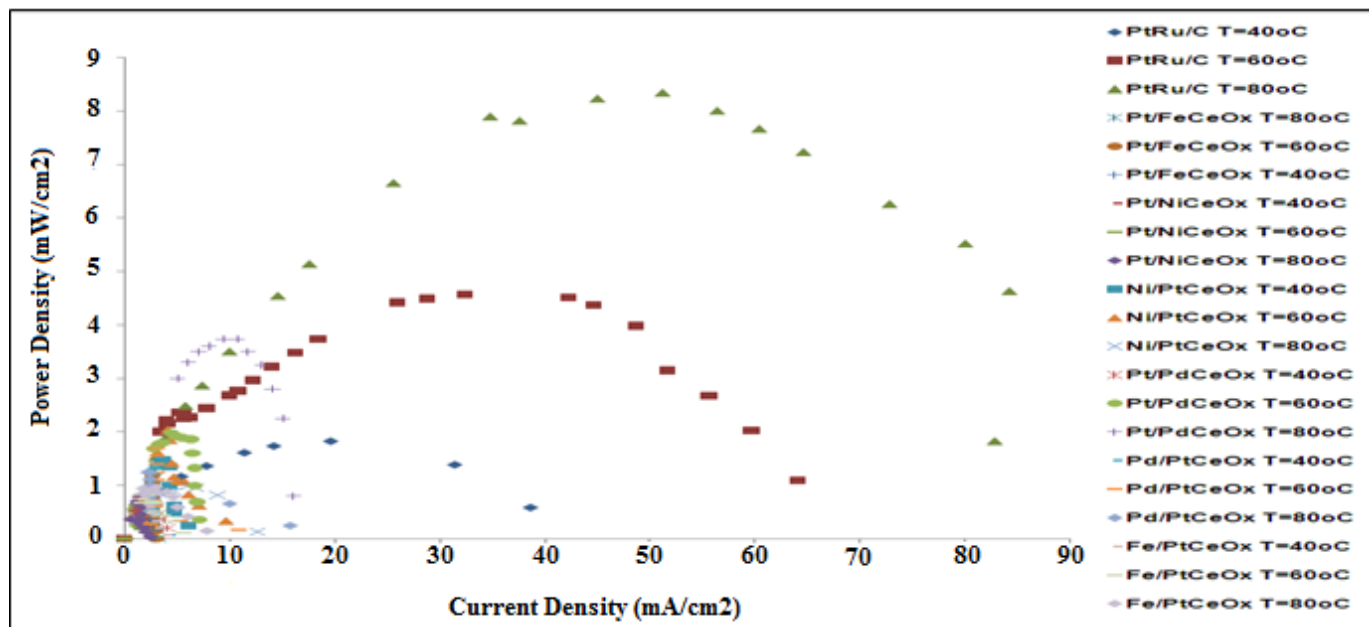


Figure 15.Power-current density curves:1M ethanol flow rate:11ml/min, Dry air flow rate: 40ml/min. Fuel cell temperatures: 40,60,80°C.

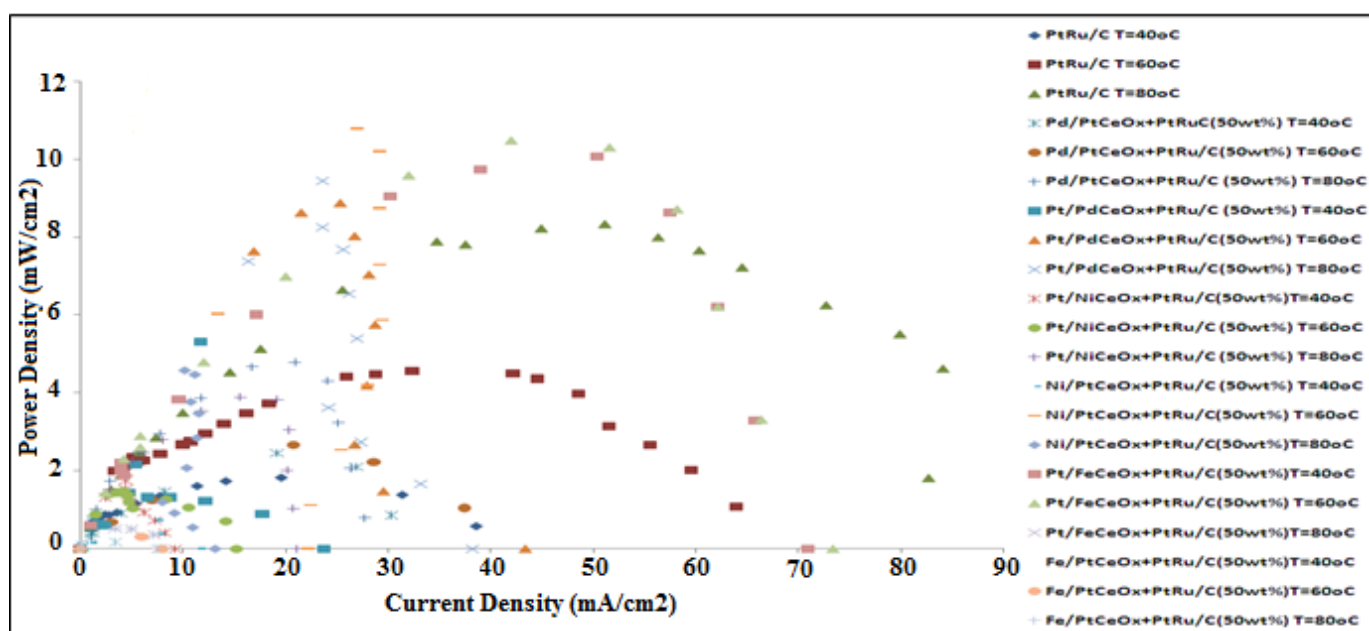


Figure 16.Power-current density curves:1M ethanol flow rate:11ml/min, Dry air flow rate: 40ml/min. Fuel cell temperatures: 40, 60, and 80°C. Comparison physically mixed catalysts with pure PtRu/C commercial catalyst.

4. CONCLUSIONS

In this study, it was possible to relate structure and activity of ceria nano-composite electro-catalysts by physical, chemical and electrochemical tests. According to the experimental results, we may conclude that Fe/PtCeOx, Pt/PdCeOx and their physical mixtures with PtRu/C showed highest

performance. When physically mixed, home-made catalysts have boosting effect and can have higher power densities than PtRu/C. The reasons of higher performance maybe due to:

- 1) The high oxygen content of Pt/PdCeO_x,
- 2) The presence of Fe₂O₃/Pt and Pt/Pd on the surface leading to bifunctional mechanism where Fe₂O₃ behave like an oxygen source to remove ethanolic and CO decomposition products,
- 3) Interaction of Pt and Pd with CeO_xmatrice forming stable structure. And facilitation of reversible electron transfer in ceria matrice by this stable structure,
- 4) Low particle size of PtCeO_x and PdCeO_x.

In addition to the reasons mentioned above, Fe/PtCeO_x and Pt/PdCeO_x showed typical ethanol electro-oxidation peaks, steady state currents higher or close to PtRu/C and overpotentials lower than PtRu/C. In these catalysts, Pt and Pd in ceria matrice are in zero valent state, and it is possible that Pt and Pd, during ethanol decomposition and oxygen transfer into the structure may change into +2 or +4 cationic state.

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