

Carbon-supported Pd–Co as cathode catalyst for APEMFCs and validation by DFT

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Carbon supported PdCo catalysts in varying atomic ratios of Pd to Co, namely 1 : 1, 2 : 1 and 3 : 1, were prepared. The oxygen reduction reaction (ORR) was studied on commercial carbon-supported Pd and carbon-supported PdCo nanocatalysts in aqueous 0.1 M KOH solution with and without methanol. The structure, dispersion, electrochemical characterization and surface area of PdCo/C were determined by X-ray diffraction (XRD), Transmission Electron Microscopy (TEM) and Cyclic Voltammetry (CV), respectively. The electrochemical activity for ORR was evaluated from Linear Sweep Voltammograms (LSV) obtained using a rotating ring disk electrode. The catalysts were evaluated for their electrocatalytic activity towards oxygen reduction reaction (ORR) in Alkaline Polymer Electrolyte Membrane Fuel Cells (APEMFCs). PdCo(3 : 1)/C gives higher performance (85 mW cm^{-2}) than PdCo(1 : 1)/C, PdCo(2 : 1)/C and Pd/C. The maximum electrocatalytic activity for ORR in the presence of methanol was observed for PdCo(3 : 1)/C. First principles calculations within the framework of density functional theory were performed to understand the origin of its catalytic activity based on the energy of adsorption of an O_2 molecule on the cluster, structural variation and charge transfer mechanism.

1. Introduction

Some of the most advanced fuel cells in terms of applications and commercialization are alkaline fuel cells (AFCs). They were used successfully in space programs in the mid 1960s. AFCs provide distinct advantages compared with polymer electrolyte membrane fuel cells (PEMFCs); in particular, the inherently faster kinetics of the oxygen reduction reaction (ORR) in AFCs allows the use of non-noble metal electrocatalysts.^{1,2} The major operating constraints for liquid AFCs are carbonation and electrolyte leakage. An anion exchange membrane (AEM) can be used as an electrolyte instead of a conventional liquid electrolyte in an AFC to avoid the above-said problems. Replacement of liquid electrolytes in conventional AFCs with metal cation free AEMs that can transfer hydroxide ions (OH^-) can revitalize the AFC technology and impart a new momentum to it and are called anion exchange polymer electrolyte membrane fuel cells (APEMFCs).^{3,4} In recent times, increasing attention has been focused on APEMFCs due to the potential usage of non-Pt catalysts, which account for the improved durability and faster ORR kinetics in alkaline medium than in acidic medium.⁵

Conventional carbon-supported platinum-based materials so far have been the most active, efficient, relevant and successful electrocatalysts for electrochemical devices at the current technology stage in acidic medium. However, in alkaline electrolyte, a wide range of non-noble metals and their oxides are stable enough for practical applications due to lower corrosion than in acidic electrolyte. This allows the investigation of a large number of non-Pt (transition metal) catalysts, especially with regard to ORR and methanol tolerance (*i.e.*, an oxygen reduction reaction selective electrocatalyst) characteristics in alkaline medium.⁶ Very high ORR catalytic activity of Pd in alkaline solution compared with Pt has been reported^{7–9} and the same has also been observed by us in our earlier study.¹⁰

In recent years, Pd and Pd alloys have attracted greater attention as non-Pt catalysts because of the high proportion of surface to bulk atoms and about 50 times more abundance of Pd than Pt.¹¹ Recent developments in using Pd and Pd-based alloys as ORR catalysts have shown promise for their use in APEMFCs.¹² The main objective of Pd-based catalyst research is the development of synthesis methods resulting in high catalytic activity of Pd. Metal based alloys have been found to exhibit higher electrocatalytic activities than pure metal.¹³ Bard *et al.* suggested that for Pd–M alloys, the metal M constitutes the site for breaking the O–O bonds.¹⁴ Incidentally, the addition of a second metal such as Co, Fe to Pd decreased the metal particle size. So alloying of Pd with transition metals (Fe, Co, Cr, Ni, Ag, *etc.*) is of significance for improving the ORR activity due to the changes in Pd–Pd bond distance, modification of electron configuration and alteration

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of surface species and composition. According to Wang and Balbuena, if a catalyst consists of two metals, one with a low occupancy of d-orbitals (such as Co, Ni, Cr, or V) and the other with fully occupied d-orbitals (such as Pd, Au, and Ag), the d-orbital coupling effect between them can significantly decrease the Gibbs free energy of the electron transfer steps in ORR, resulting in an enhancement in ORR kinetics.¹⁵ Fernandez explained that, thermodynamically, a PdCo alloy is the most promising binary system compared with AuCo and AgCo in regard to the catalytic activity.¹³ In low pH media, dissolution of the transition-metal-alloyed catalysts is a major drawback because these transition metals are electrochemically soluble at a potential range of 0.3–1 V *vs.* NHE.¹⁶ In acidic medium, it is found through XPS studies that Co dissolves as cobalt oxides, while in alkaline medium it is stable.¹⁷ Zhang *et al.*¹⁸ have reported that the optimal heat-treatment temperature for the synthesis of Pd–Co alloys is 300 °C.

In the present study, the catalytic activity of carbon-supported PdCo catalysts in varying atomic ratios is evaluated for ORR with and without methanol in half-cell mode and by the polarization studies in fuel cell mode with hydrogen as a fuel and oxygen or air as an oxidant. The identification of crystal phases through X-ray diffraction (XRD) and the dispersion of the catalyst by the Transmission Electronic Microscopy (TEM) were studied. The electrocatalytic activity towards ORR with and without methanol in alkaline solution was investigated by Cyclic Voltammetry (CV), Linear Sweep Voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). Based on band gap and bond length the catalysts were analysed by DFT calculations.

2. Experimental section

2.1. Preparation of catalyst

Procedure for preparation of palladium–cobalt on carbon support by sodium borohydride reduction method reported in the literature¹⁹ was followed. For preparation of 1 : 1 PdCo/C, 110 mg of cobalt chloride (Aldrich) was dissolved in water. Commercially available 20% Pd/C (Alfa Aesar) was wet with IPA before addition of water and sonicated for half-an-hour to make a homogeneous solution. To this solution, cobalt chloride solution was added with constant stirring followed by the addition of 50 ml of 0.5 M sodium borohydride. However, before the addition of sodium borohydride, the pH was adjusted to be alkaline with a few drops of 1 M NaOH solution. The mixture was constantly stirred for 1 hour. Further, the mixture was filtered, washed with deionized water, and dried in an oven at 80 °C overnight. The obtained carbon-supported PdCo was ground to make a fine catalyst powder and the powder was placed in a tubular furnace and nitrogen gas was allowed to flow into the furnace at a rate of 200 ml min^{−1} for 2 h to remove any residual air before increasing the temperature. The powder was then heat treated at 300 °C under constant flow of a mixture of nitrogen and hydrogen (3 : 1 ratio) for 2 h with a ramp rate of 2 °C min^{−1} and subsequently cooled to room temperature, thus forming a carbon-supported PdCo alloy catalyst.

Hereafter in the following text, the carbon-supported PdCo (PdCo/C) samples with varying atomic ratios of Pd to Co,

namely, 1 : 1, 2 : 1, and 3 : 1, will be denoted PdCo(1 : 1)/C, PdCo(2 : 1)/C and PdCo(3 : 1)/C, respectively.

2.2. Physical characterization

Powder XRD studies were conducted to analyze the crystallinity of carbon-supported PdCo nanocatalysts. For this purpose, powder XRD patterns were obtained on a Philips X'Pert Diffractometer using CuK α radiation (λ = 1.5406 Å) between 10° and 90° in reflection geometry in steps of 0.017° s^{−1}.

A transmission electron microscope was used to determine the average particle size and dispersion of carbon supported PdCo catalysts. For this purpose, the microscopic features of the samples were examined by using a TCNAI 20 G2 transmission electron microscope (200 kV). For TEM characterization, a carbon film deposited onto a mica sheet was placed onto a copper grid. The catalyst was suspended in isopropyl alcohol and cast by dropping the suspension onto the carbon-coated copper grid followed by solvent evaporation in vacuum at room temperature ($\sim$ 25 °C).

Inductively coupled plasma-optical emission spectrometry (ICP-OES) was used to analyze the bulk Pd and varying ratios of Pd to Co in PdCo/C. For this purpose, the catalysts were dissolved in aqua regia followed by dilution with water to concentration ranging between 1 and 100 ppm as desired for the analysis. The actual composition was determined from the calibration curves of known standards. The surface atomic compositions of various PdCo/C catalysts were obtained using energy dispersive X-ray analysis (EDAX) (Thermo electron corporation) facility provided with a scanning electron microscope (HITACHI S-3000 H, Japan).

2.3. Electrochemical characterization

2.3.1. Cyclic voltammetry and LSV experiments. All the catalysts were electrochemically characterized using Cyclic Voltammetry (CV) and ORR was evaluated based on the linear-sweep voltammetry (LSV) measurements. The electrochemical setup consisted of a computer-controlled electrochemical analyzer (Autolab PGSTAT-30), a radiometer speed control unit from Pine Instrument Company (MSRX Speed control) and a rotating ring disk electrode (glassy carbon disk of 5 mm diameter and platinum as the ring). A conventional three-electrode cell consisting of a glassy carbon (GC) disk with a geometric area of 0.196 cm² was used as the working electrode. Before each test, the electrode was polished with 0.06 μ m alumina on a polishing cloth to obtain a mirror-like finish followed by rinsing with double-distilled water in an ultrasonic bath. For ink preparation, 14 mg of catalyst and 10% Nafion ionomer were ultrasonically dispersed with 4 ml of water for 30 min to obtain a homogeneous solution. In this case, Nafion helps to attach the catalyst particles on the GC electrode.²⁰ To prepare the working electrode, catalyst (Pd/C, PdCo(1 : 1)/C, PdCo(2 : 1)/C, PdCo(3 : 1)/C) suspension was quantitatively transferred to the surface of polished GC disk. The electrode was dried at room temperature. A pre-calibrated Mercury Mercuric Oxide (MMO, 0.165 V *vs.* standard hydrogen electrode) electrode and a platinised Pt foil were used as the reference and counter electrodes, respectively, in the three-electrode configuration. All electrochemical experiments were carried out at room temperature ($\sim$ 25 °C).

Hydrogen peroxide production in the O₂ saturated 0.1 M KOH electrolyte was monitored using a polycrystalline platinum ring biased at 0.5 V vs. MMO, in RRDE configuration. Collection efficiency of the Pt ring electrode is $N = i_{\text{ring}}/i_{\text{disk}} = 0.35$.

In order to clean and activate the working electrode, it was cycled between -0.9 and 0.5 V with respect to MMO at a sweep rate of 50 mV s⁻¹ in high pure nitrogen purged 0.1 M KOH with and without 0.1 M CH₃OH until stable and reproducible voltammograms were obtained. The cyclic voltammograms were recorded once the working electrode was well equilibrated. LSV experiments were performed using RRDE in oxygen saturated 0.1 M KOH with and without 0.1 M CH₃OH. LSV data were recorded in the cathodic-sweep direction from 0.2 V to -0.5 V vs. MMO over a range of rotations (400 to 2400 rpm) at a scan rate of 3 mV s⁻¹.

2.4. Fuel cell studies

2.4.1. Customizing the electrolyte. Ammonium-type anion exchange membrane (AHA-Neosepta) was modified from Cl⁻ to OH⁻ form as follows. The AHA membrane comprises tetra-alkyl ammonium groups as fixed cation groups bonded to a polyolefin backbone chain. The Cl⁻ form membrane was rinsed several times with de-ionized water, and then immersed in 4 mol dm⁻³ KOH aqueous solution at room temperature overnight for the replacement of Cl⁻ with OH⁻. The membranes were again washed several times with de-ionized water at room temperature.

2.4.2. Fabrication of membrane electrode assembly (MEA). MEA preparation for APEMFCs was already described elsewhere¹⁰ with some modification. In brief, both electrodes comprised a backing layer, a gas diffusion layer and a catalyst layer. For backing layer, carbon paper (Toray TGP-H-120) of 0.35 mm thickness was teflonised with 15 wt% of polytetrafluoroethylene (PTFE) emulsion and sintered at 350 °C for one hour. The Gas Diffusion Layer (GDL) was coated with a homogeneous suspension of high surface area carbon (Vulcan XC72 R) with 1.5 mg cm⁻² loading over the teflonised Toray sheet, which was then sintered at 350 °C for half-an-hour.

2.4.2.1. Preparation of anode catalyst layer. To prepare the anode catalyst layer, 44.2 mg of 38% Pt/C (Johnson Matthey Corp.), was suspended in isopropyl alcohol. The mixture was agitated in an ultrasonic water bath, and 15 wt% of PTFE emulsion that acts as a binder was added to the solution. The resulting ink was coated on GDL and sintered for 15 min.

2.4.2.2. Preparation of cathode catalyst layer. PdCo/C comprising Pd and Co in varying ratios was suspended in Dimethyl Acetamide (DMAc) and the mixture was agitated in an ultrasonic water bath. 15 wt% of anion conducting ionomer FAA (I&II in 6 : 1 ratio) (Fumatech, Germany) was dissolved in DMAc and added to the catalyst slurry. The mixture was treated ultrasonically for at least 10 min and then coated on GDL, and kept in 2 M KOH solution for 4 h for cross linking of the ionomer. The ionomer was added only to the cathode slurry with continuous ultrasonication.¹⁰ Both anode and cathode contained metal/alloy loading of 0.5 mg cm⁻² (active area 25 cm²), which was kept identical in all the MEAs. MEAs were obtained by pressing the cathode and anode on either side of the anion

exchange membrane under a compaction pressure of 60 kg cm⁻² at room temperature for 5 min.

2.4.3. Cell polarization studies. The performance of MEAs was evaluated using a conventional 25 cm² fuel cell fixture with a parallel serpentine flow field machined on graphite plates (Schunk Kohlenstofftechnik GmbH, Germany). After equilibration, the single cells were tested at room temperature (30 °C) with humidified hydrogen and oxygen at anode and cathode, respectively, at a flow rate of 0.5 l min⁻¹ at atmospheric pressure. Measurements of cell potential as a function of current density were conducted potentiostatically using a LCN10-40 electronic load procured from Bitrode Corporation.

2.5. AC impedance measurement

A frequency response analyser was used to measure the polarisation resistance of MEAs at 0.8 V. The reference and counter electrode leads were connected to a hydrogen electrode and working electrode lead was linked to an air electrode. The impedance measurements were conducted in the frequency range of 10 kHz to 100 kHz by imposing a single sinusoidal wave with an amplitude of 10 mV.

2.6. X-ray photoelectron spectroscopy

The XPS for the catalysts was recorded on a Multilab 2000 (ThermoFisher Scientific, U.K) X-ray photoelectron spectrometer fitted with a twin anode X-ray source using Mg K α radiation (1253.6 eV). For recording the desired spectrum, the powder sample was pressed onto a conducting carbon tape pasted with indium coated stainless steel stubs. The sample stubs were initially kept in the preparatory chamber overnight at 10⁻⁹ mbar to desorb any volatile species and then introduced into the analysis chamber at 9.8×10^{-10} mbar to record the spectra. High resolution spectra averaged over five scans with a dwell time of 100 ms in steps of 0.02 eV were obtained for the catalyst samples at a pass energy of 20 eV in the constant analyzer energy mode. Experimental data were curve fitted with a Gaussian and Lorentzian mix product function after subtracting the Shirley background. The spin-orbit splitting and the doublet intensities were fixed as described in the literature.²¹ Relative intensities for the surface species were estimated from the respective areas of the fitted peaks.

2.7. Computational methodology

In order to understand the experimentally observed catalytic behavior of Pd-Co binary clusters, first principles calculations were performed. A tetrahedral Pd₄ cluster was considered for this study as this isomer is known to be stable.²² Further Co atoms were introduced in this cluster in order to mimic the binary clusters. Atomic and catalytic properties of Pd₄, Pd₃Co, Pd₂Co₂, PdCo₃, and Co₄ clusters were calculated within the framework of density functional theory as implemented in VASP.²³ Plane wave based ultrasoft pseudopotentials^{24,25} were used to describe the interactions between the Pd_nCo_{4-n} cluster and an O₂ molecule. The exchange-correlation energy in the system was corrected by generalized gradient approximations.²⁶ The bare clusters were kept in a large cubic supercell of 18 Å. Due to the presence of Co atoms, the spin-polarized calculations were performed. All ions were optimized without restricting any

symmetry and the optimization process was repeated until the force constant of each atom converged to ± 10 meV $\text{\AA}^{-1}$. To understand the catalytic properties of these clusters, an O_2 molecule was allowed to adsorb on various sites of these clusters. The adsorption energy (E_{ads}) was calculated from

$$E_{\text{ads}} = E(\text{Pd}_n\text{Co}_{4-n}) + E(\text{O}_2) - E(\text{Pd}_n\text{Co}_{4-n}/\text{O}_2)$$

where $E(\text{Pd}_n\text{Co}_{4-n})$ is the total energy of the $\text{Pd}_n\text{Co}_{4-n}$ cluster, $E(\text{O}_2)$ is the total energy of the O_2 molecule, and $E(\text{Pd}_n\text{Co}_{4-n}/\text{O}_2)$ is the total energy of O_2 adsorbed $\text{Pd}_n\text{Co}_{4-n}$ clusters, respectively.

To understand the charge transfer between the cluster and the molecule, we deduced the excess and depletion charge densities ($\Delta\rho$) from

$$\Delta\rho = \rho(\text{cluster} + \text{molecule}) - \rho(\text{cluster}) - \rho(\text{molecule})$$

where $\rho(\text{cluster} + \text{molecule})$, $\rho(\text{cluster})$, and $\rho(\text{molecule})$ are the total charge density of the O_2 molecule adsorbed cluster, isolated cluster, and the O_2 molecule, respectively.

3. Results and discussion

The composition of the PdCo/C catalysts was analysed by ICP-OES and the results are presented in Table 1. The compositions of the prepared PdCo/C bimetallic catalysts are found to be nearly the same as the stoichiometric values, confirming the presence of Co in the alloy. The composition of the alloys analysed by EDAX also agrees with the values obtained by ICP-OES.

3.1. X-ray diffraction

The crystalline structures of PdCo/C catalysts with Pd and Co in varying ratios are characterized by XRD and shown in Fig. 1. For comparative purposes, the XRD pattern of commercial 20 wt% of Pd/C is also included in the figure. The diffraction peaks at 2θ values of 40.1° , 46.68° , 68.08° and 82.0° are due to the (111), (200), (220) and (311), respectively, for the crystalline planes of Pd/C with a face centered cubic (fcc) structure in conformity with The American Mineralogist Crystal Structure Database (database code amcsd 0011155). These four diffraction peaks for the PdCo/C bimetallic catalysts are shifted slightly to higher 2θ values (Table 1) with respect to the corresponding peaks in the Pd/C catalyst. This confirms the alloy formation between Pd and Co and indicates lattice contraction, which is caused by the incorporation of Co into the Pd fcc structure. Since no characteristic peak of pure Co and its oxides is found in the XRD pattern, this indicates that PdCo/C is in the alloy form. The mean particle sizes are calculated from the (111) diffraction line using the Scherrer equation.

$$d = \frac{0.94\lambda_{kxz}}{\beta \cos\theta} \quad (1)$$

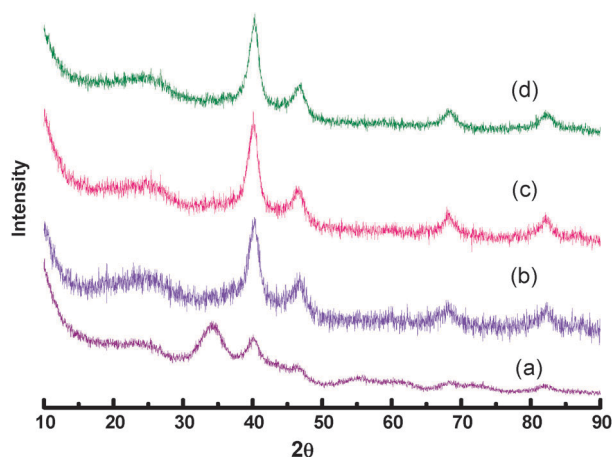


Fig. 1 XRD patterns of (a) Pd/C, (b) PdCo(1 : 1)/C, (c) PdCo(2 : 1)/C and (d) PdCo(3 : 1)/C.

where d is the average particle diameter, λ_{kxz} is the wavelength of the X-ray radiation (1.5406 $\text{\AA}$), β is the full width at half-maximum (fwhm, in radian) of the diffraction peak and $\cos\theta$ is the Bragg angle for the (111) peak. The particle sizes of Pd/C, PdCo(1 : 1)/C, PdCo(2 : 1)/C and PdCo(3 : 1)/C are 3.2, 4.0, 4.25 and 5.3 nm, respectively. From the crystallite size data, it is clear that the mean crystallite size increases with decreasing Co content due to the lattice parameter and average Pd–Pd bond distance increases with decreasing Co content. The lattice parameters obtained for all the prepared Pd–Co/C catalysts are smaller than that of Pd/C and show a decrease with increase in Co content, indicating lattice contraction upon alloying.

The formation of the alloy can induce Pd lattice compression (or reduction of bond lengths between metals) through the modification of the electronic structure and orbital overlap. This will cause the shift of the d-band center, resulting in a change in the surface activity of Pd sites. It is confirmed through the density functional theory calculations that the compression of a metal lattice in alloys could downshift the d-band center energy and can enhance the catalyzed ORR.²⁷

3.2. Catalyst morphology

The TEM images of PdCo(1 : 1)/C, PdCo(2 : 1)/C and PdCo(3 : 1)/C alloy catalysts are shown in Fig. 2a–c, respectively. It can be seen that all the nanoparticles are crystalline and are uniformly dispersed on carbon. The mean particle size decreases with increasing Co content in the alloy. This indicates that Co hinders the aggregation of particles.

The mean particle diameter (d) calculated using the formula $d = \frac{(\sum n_i d_i)}{n_i}$, where n_i is the frequency of occurrence of particles of diameter, d_i , are 3.80, 4.17 and 5.20 nm for PdCo/C catalysts

Table 1 Compositions and structural parameters for the Pd/C and PdCo/C catalysts with varying Pd and Co ratios

Catalyst	2θ (111)	Pd–Pd bond distance/nm	Lattice parameter/nm	Electrochemical surface area/ $\text{m}^2 \text{g}^{-1}$	Pd to Co atomic ratio in EDAX	Pd to Co atomic ratio in ICP-OES	Particle size (nm) XRD
Pd/C	40.1	0.284	0.405	82.38	—	—	3.2
PdCo/C 1 : 1	40.39	0.270	0.381	54.76	55.78 : 44.22	57.34 : 42.66	4.0
PdCo/C 2 : 1	40.51	0.275	0.389	70.14	66.92 : 33.08	64.29 : 35.71	4.25
PdCo/C 3 : 1	40.55	0.278	0.395	78.82	71.17 : 28.83	74.24 : 25.76	5.3

containing Pd and Co in 1 : 1, 2 : 1 and 3 : 1, respectively. In this study, the mean size of the palladium–cobalt nanoparticles on carbon support is obtained by measuring 200 randomly chosen particles in the magnified TEM images. The particle sizes of the catalysts are in good agreement with the data obtained from XRD. Inset to Fig. 2(a)–(c) show the electron

diffraction of respective TEM images of the catalyst. The clear ring patterns confirm the crystallinity of the particles.

As the particle size increases, there should be an increase in the number of metal atoms on various crystal facets with respect to those at edges and corners. Under the operating conditions of fuel cell, especially in the presence of electric

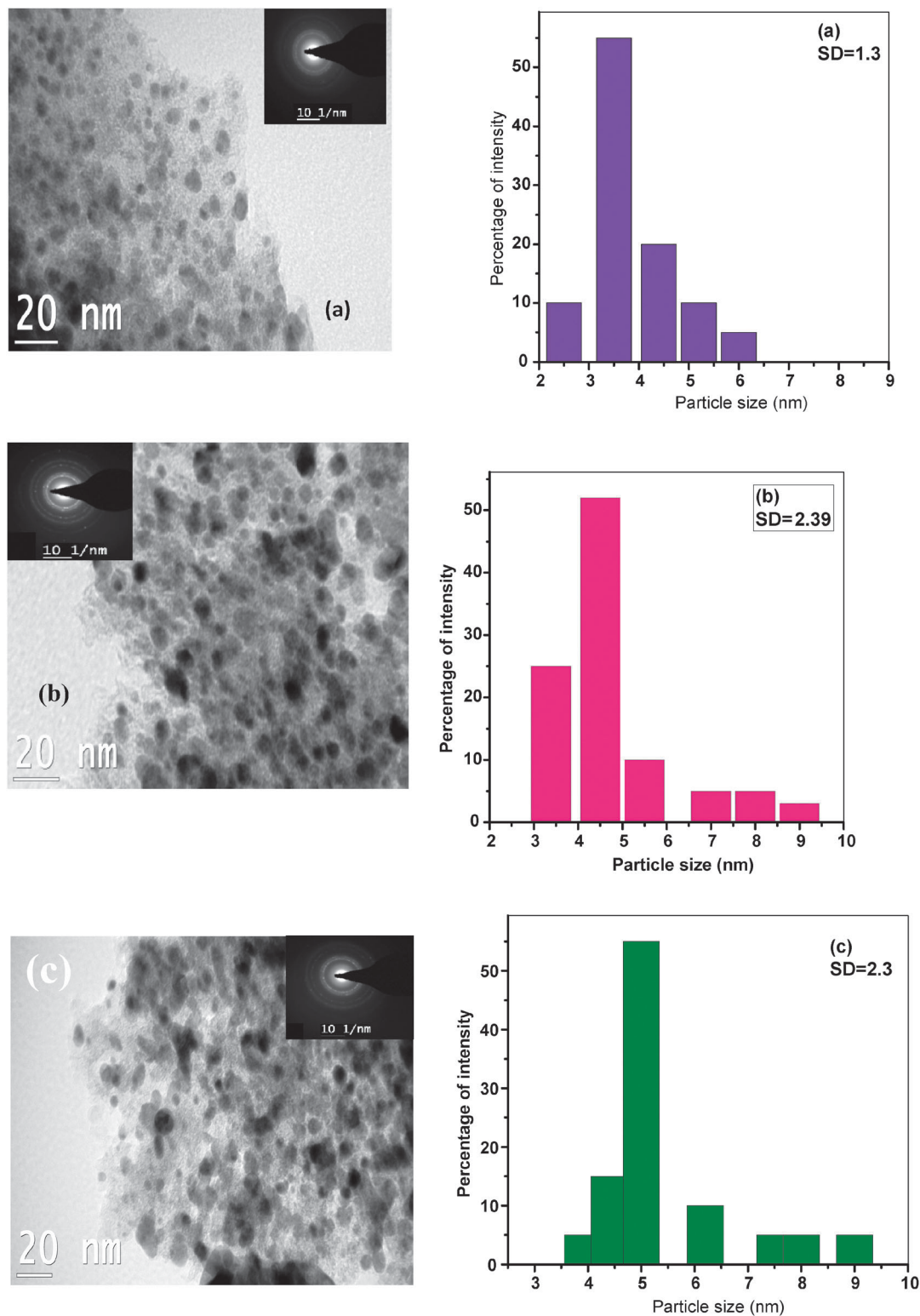


Fig. 2 TEM images and the corresponding particle size distribution histograms for (a) PdCo(1 : 1)/C, (b) PdCo(2 : 1)/C and (c) PdCo(3 : 1)/C.

potential there should be a drastic change in the geometries, charges and adsorption energies of the species on a catalyst surface. As a result, population of the antibonding $2\pi^*$ orbitals in the oxygen molecule increases and facilitates the reduction of oxygen to water.²⁸

3.3. Electrochemical characterization

Fig. 3 shows the cyclic voltammograms of Pd and PdCo/C catalysts containing Pd and Co in varying atomic ratios in high pure nitrogen saturated 0.1 M KOH solution at 25 °C. In the forward scan the Pd/C electrocatalyst exhibited a large hydrogen peak below -0.6 V vs. MMO. This large peak is caused by dissolution of the adsorbed hydrogen into the bulk of the Pd electrode. All the Pd alloy electrocatalysts showed much smaller hydrogen peaks below -0.6 V vs. MMO compared with the Pd electrode due to restrained hydrogen dissolution.

The real surface area of the Pt electrocatalyst is normally evaluated from the hydrogen desorption peak of the cyclic voltammogram. In contrast to Pt, it is difficult to determine the charge of a monolayer of adsorbed hydrogen on Pd and Pd alloy due to its dissolution into the bulk of palladium (at ambient conditions palladium can absorb up to 900 times its own volume of hydrogen). For the determination of Pd real surface area, the ESA is calculated from the charge corresponding to the reduction of oxide,²⁹ which is formed due to adsorption of a monolayer of chemisorbed oxygen and is two times as large as that ($Q_H = 210 \mu\text{C cm}^{-2}$) of the hydrogen monolayer, *i.e.* ($Q_H = 1/2Q$).³⁰ *i.e.*,

$$\text{ESA}(\text{cm}^2 \text{mg}_{\text{Pd}}^{-1}) = \frac{Q_O(\mu\text{C cm}^{-2})}{420 \mu\text{C cm}^{-2} \times \text{electrode loading}(\text{mg}_{\text{Pd}} \text{cm}^{-2})} \quad (2)$$

ESA values for all the samples are presented in Table 1. Pd/C has higher ESA than PdCo(3 : 1)/C, which is attributed to increase the particle size upon heat treatment. Among other catalysts, PdCo(3 : 1)/C shows higher ESA compared with PdCo(2 : 1)/C and PdCo(1 : 1)/C. It clearly shows that higher amount of Co may hinder the electrocatalytic activity of Pd *i.e.*, larger quantity of Co may encapsulate the Pd active sites.

In the reverse scan oxide reduction peak potential shifts to more positive potentials with increasing Co content. For pure

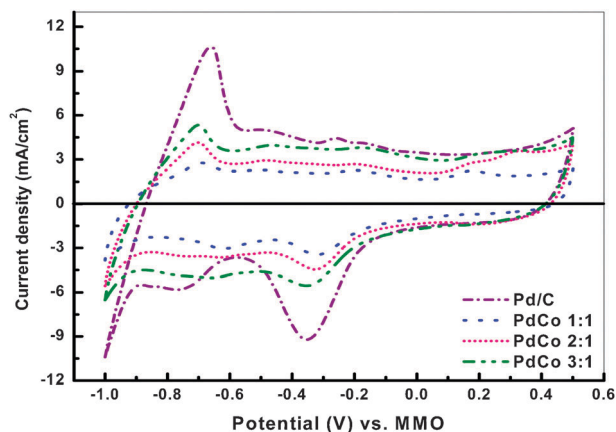


Fig. 3 Steady state cyclic voltammograms of Pd/C, PdCo(1 : 1)/C, PdCo(2 : 1)/C and PdCo(3 : 1)/C in deaerated 0.1 M KOH at a sweep rate of 50 mV s^{-1} .

Pd, oxide reduction peak in the cathodic going sweep is at -0.358 V vs. MMO, whereas on carbon-supported catalysts containing Pd and Co in varying ratios of 1 : 1, 2 : 1 and 3 : 1 the corresponding potential is observed at -0.315 , -0.325 and -0.350 V vs. MMO, respectively. This indicates that alloying with Co effects a fundamental change in Pd atoms and its interaction with H_2O and possibly O_2 . This change could be manifested in the kinetic measurements. It is interesting to note that the trend observed in electrochemical surface area with respect to changing composition of the alloy namely the decrease in surface area with increase in Co content is similar to that reported³¹ for PtCo alloy in alkaline solutions. The decrease in ECSA with increasing Co content in the alloys is attributed to the formation of stable Co oxide/Co hydroxide species on the surface.

3.4. Electrochemical characterisations

Fig. 4(a) shows the linear sweep voltammograms on the Pd alloy electrocatalysts in oxygen saturated 0.1 M KOH solution at a rotation rate of 1600 rpm and at a scan rate of 3 mV s^{-1} (current is normalized with reference to geometric area of the working electrode), and compared with Pd/C. PdCo(3 : 1)/C shows higher onset potential of ~ 40 mV and half-wave potential compared with Pd/C. PdCo(3 : 1)/C shows better catalytic activity than Pd/C, PdCo(2 : 1)/C and PdCo(1 : 1)/C. Measurable ring currents are observed as shown in Fig. 4(b) in the potential region of diffusion control (*i.e.* above -0.075 V vs. MMO). The behavior of ring response clearly denotes formation of HO_2^- as an intermediate of the ORR. A sharp peak observed at -0.15 V vs. MMO is due to peroxide oxidation in 0.1 M KOH. The sharp increase in the ring current at -0.15 V during ORR in alkaline media is closely related to $-\text{OH}$ formation from the specific adsorption of hydroxide anions.³² These results clearly show that lower quantities of peroxide ions are formed for PdCo(3 : 1)/C than Pd/C, PdCo(2 : 1)/C and PdCo(1 : 1)/C. The enhanced activity of PdCo(3 : 1)/C may be due to lowering of the Palladium d-band center due to cobalt present in the alloy.³³

Fig. 5 shows the current density for the ORR at -0.05 V vs. MMO as a function of the alloy composition. The highest electrocatalytic activity was observed for the alloy composition of *ca.* 75 atom% Pd in the Pd alloy. This is in good agreement with the previous reports in which the highest activity was reported for 80–70 atom% Pd in the PdCo alloy.^{14,34} The lower electrocatalytic activity on PdCo(1 : 1)/C and PdCo(2 : 1)/C is probably due to the fact that higher Co content within a catalyst sample results in Co surface enrichment, which may encapsulate the active sites of Pd and is not favorable for adsorption of oxygen molecules on a palladium atom.

Fig. 6 shows Tafel plots for ORR on Pd alloys in comparison with Pd. The i_k values are determined from the following equation.

$$i_k = (i_d^* i)/(i_d - i) \quad (3)$$

where i_k , i_d and i are the exchange current density, the diffusion limiting current density and the observed current density, respectively. Two Tafel slope regions, *i.e.*, *ca.* -60 mV dec^{-1} and -120 mV dec^{-1} are observed for all the electrocatalysts.

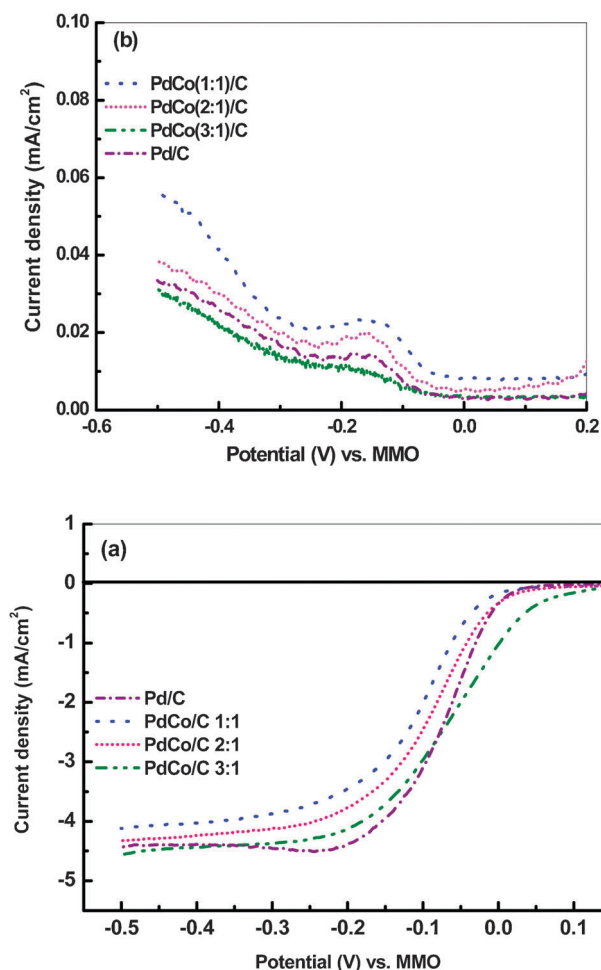


Fig. 4 (a) Linear sweep voltammograms of Pd/C, PdCo(1 : 1)/C, PdCo(2 : 1)/C and PdCo(3 : 1)/C in oxygen saturated 0.1 M KOH solution at 1600 rpm. (b) Ring current measured during ORR at 1600 rpm.

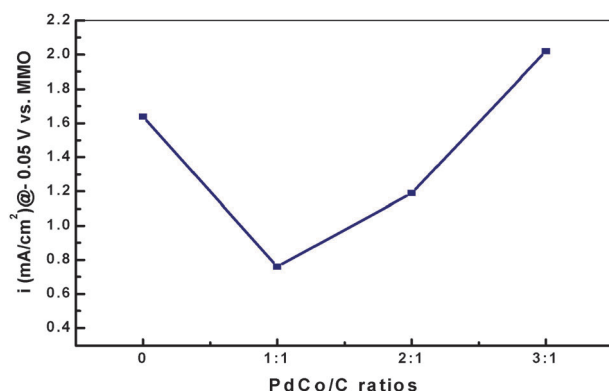


Fig. 5 ORR current density at -0.05 V vs. MMO as a function of alloy composition.

The transition of the Tafel slope from low to high value region is attributed to the formation of oxides from the reaction of H_2O with Pd.³⁴ For the Pd electrocatalyst, the low and high Tafel slopes are -65 and -119 mV dec^{-1} , respectively. This result is in good agreement with the literature.^{7,34} The Tafel slopes obtained at low overpotential (*i.e.*, $-0.15 < E < 0$)

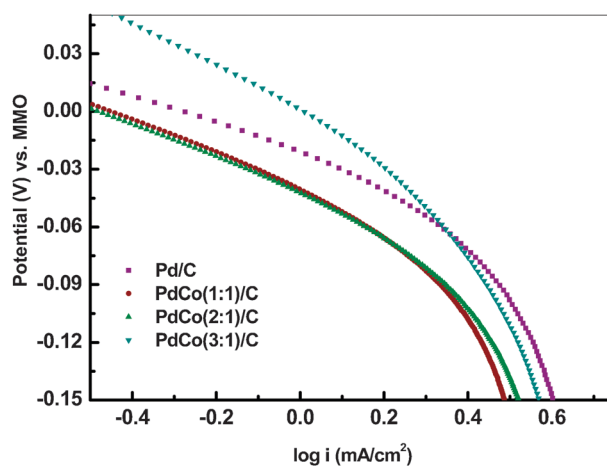


Fig. 6 Tafel plots of Pd/C, PdCo(1 : 1)/C, PdCo(2 : 1)/C and PdCo(3 : 1)/C.

from the above plot are given in Table 2. The Tafel slope values follow the same order namely PdCo (3 : 1) > PdCo (2 : 1) > PdCo (1 : 1) with respect to ORR activity as revealed by half-wave potential values presented in Table 2. The reverse trend is also in agreement with shift in the potential of Pd oxide formation, which affects the ORR kinetics, as observed in CV.³⁴

To calculate the kinetic current of the catalyst, cathodic limiting current-densities are plotted vs. $\omega^{1/2}$ and a slightly curved line (not shown) is observed. Hence, in order to eliminate the kinetic influence, the Koutecký–Levich (K–L) plots are drawn based on the K–L equation *viz.*

$$1/i = 1/i_k + 1/i_d \quad (4)$$

$$1/i = 1/i_k + 1/(B\omega^{1/2}) \quad (5)$$

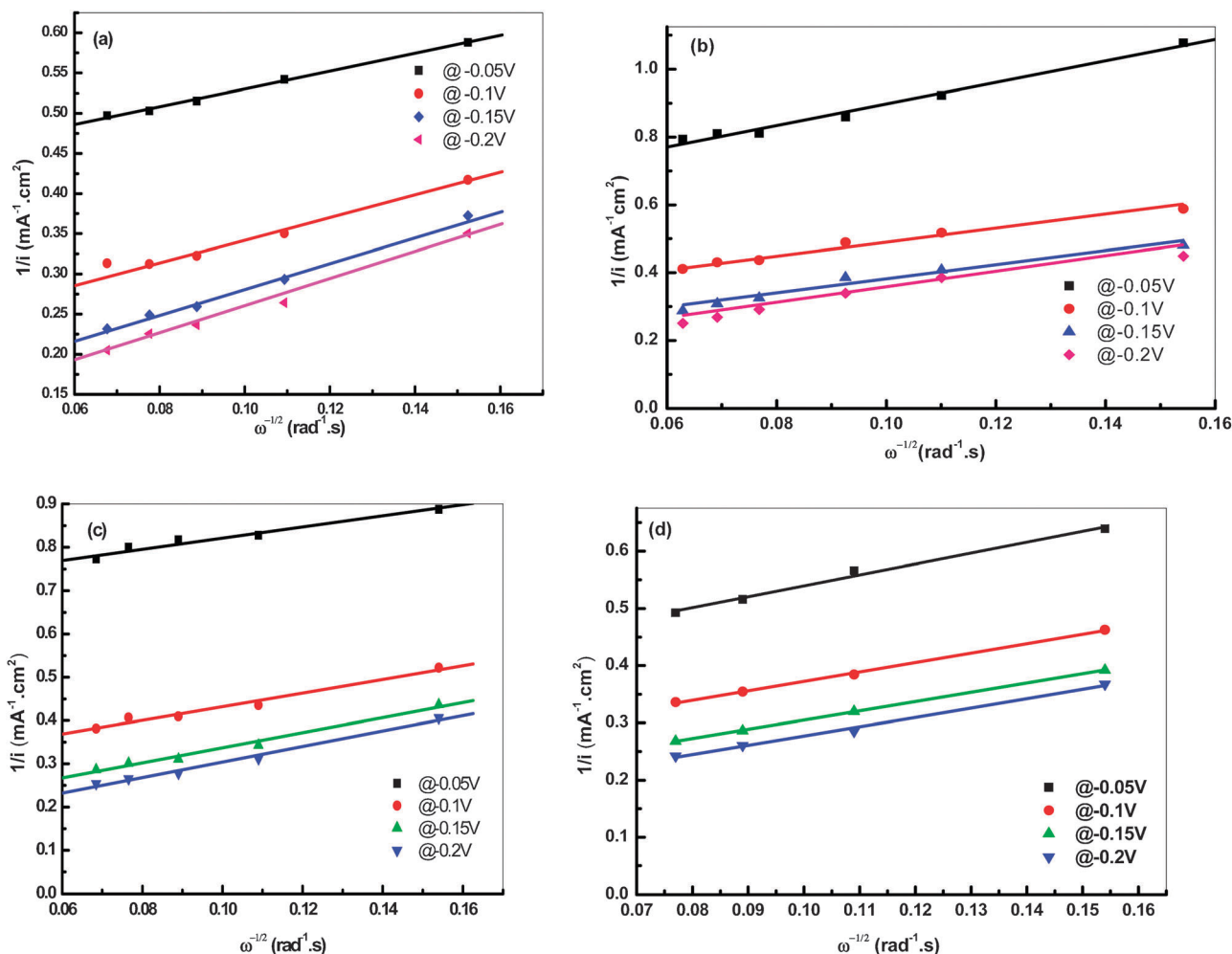
where ' ω ' is rotation rate in radian. A plot of $1/i$ (at -0.05 , -0.1 , -0.15 and -0.2 V vs. MMO) vs. $1/\omega^{1/2}$ as shown in Fig. 7 is linear and on extrapolation to $\omega^{-1/2} = 0$ yields $1/i_k$.³⁵ The i_k values obtained at -0.05 and -0.1 V vs. MMO are given in Table 2 and these values are higher for the PdCo(3 : 1)/C catalyst than that for Pd/C, PdCo(2 : 1)/C and PdCo(1 : 1) in accordance with their catalytic activities.

3.5. Cell polarisation studies

Steady state polarization studies are conducted for APEMFCs comprising Pd/C, PdCo(3 : 1)/C, PdCo(2 : 1)/C and PdCo(1 : 1)/C as cathode catalysts with a metal/alloy loading of 0.5 mg cm^{-2} and 38% Pt/C as anode catalyst with a loading of 0.5 mg cm^{-2} at room temperature. Fig. 8 shows steady-state performance curves for APEMFCs with Pd/C, PdCo(3 : 1)/C, PdCo(2 : 1)/C and PdCo(1 : 1)/C as cathode catalysts with hydrogen and oxygen as fuel and oxidant, respectively. Among the various APEMFCs, the cell comprising PdCo(3 : 1)/C shows the highest peak power density of 85 mW cm^{-2} in relation to PdCo(2 : 1)/C, Pd/C and PdCo(1 : 1)/C with a power density of 75, 56 and 26 mW cm^{-2} , respectively. The peak power densities of APEMFCs comprising PdCo(3 : 1)/C, PdCo(2 : 1)/C, Pd/C and PdCo(1 : 1)/C as cathode catalysts and Pt/C as anode catalyst and operating with hydrogen as a fuel and air as an oxidant at room

Table 2 Parameters derived from hydrodynamic polarization curves of ORR

Catalyst	Onset potential (mV) ± 0.2	Kinetic current density (mA cm ⁻²) ± 0.002		Mass activity @ -0.05 V vs. MMO (mA mg ⁻¹)	Half wave potential (E _{1/2}) (mV) ± 0.3	Tafel slope value (mV dec ⁻¹) ± 1
		@ -0.05 V	@ -0.1 V			
PdCo(1 : 1)/C	7	1.293	2.440	10.59	-100	70
PdCo(2 : 1)/C	33	1.300	2.73	16.90	-85	63
PdCo (3 : 1)/C	79	2.071	3.055	28.32	-59	60
Pd/C	30	2.057	3.040	23.61	-66	65

**Fig. 7** K–L Plots of (a) Pd/C (b) PdCo(1 : 1)/C (c) PdCo(2 : 1)/C and (d) PdCo(3 : 1)/C at -0.05, -0.1, -0.15 and -0.2 V vs. MMO at different rpm.

temperature are 37, 26, 19 and 11 mW cm⁻², respectively, as shown in Fig. 9. The polarization values are found to corroborate well with the trend observed in the kinetic studies.

Fig. 10 shows the stability in performance of APEMFC comprising PdCo(3 : 1)/C as cathode catalyst over 80 h employing hydrogen as a fuel and air as an oxidant at room temperature and at a constant potential of 0.6 V.

Fig. 11 shows the electrochemical impedance spectra for APEMFCs obtained at an operating cell voltage of 0.8 V. The high-frequency intercept with the real axis represents the ionic resistance of the electrolyte (R_s). The impedance spectrum at low frequencies shows polarization resistance (R_p), which is a combination of charge-transfer and diffusion resistances.

Generally, the charge-transfer resistance dominates the diffusion resistance at low load current densities. The diameter of the semicircle decreases in the order of PdCo(1 : 1)/C > Pd/C > PdCo(2 : 1)/C > PdCo(3 : 1)/C. The reduction in the charge-transfer resistance of PdCo(3 : 1)/C in relation to PdCo(1 : 1)/C, PdCo(2 : 1)/C and Pd/C indicates that APEMFC comprising PdCo(3 : 1)/C shows higher ORR activity in comparison to other catalysts. These data are in good agreement with cell polarization studies (Fig. 8). In general, unlike PEMFC, the APEMFC impedance results cannot be directly correlated to ORR activity, because in the case of the former the anode polarization loss is almost negligible even at high current density. In the case of APEMFC, the anode is relatively highly polarizable and, hence,

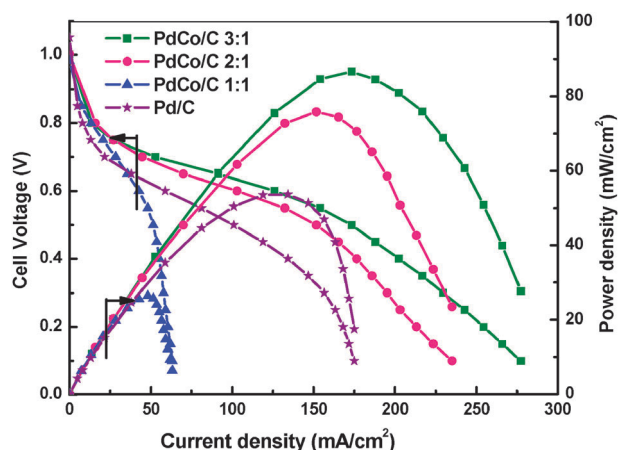


Fig. 8 Steady state performance curves for APEMFCs (hydrogen and oxygen) comprising Pd/C, PdCo(1 : 1)/C, PdCo(2 : 1)/C and PdCo(3 : 1)/C as cathode catalysts at room temperature.

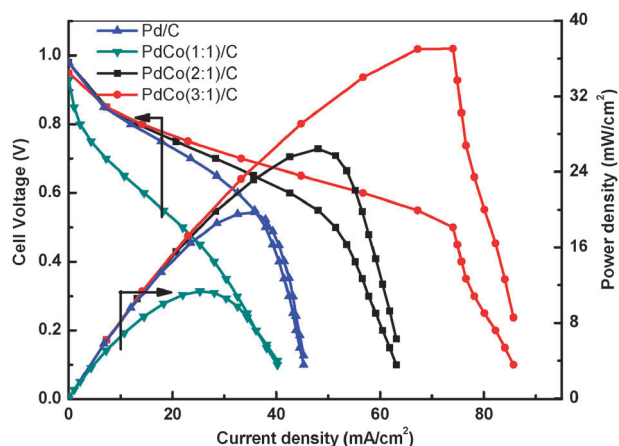


Fig. 9 Steady state performance curves for APEMFCs (hydrogen and air) comprising PdCo(1 : 1)/C, PdCo(2 : 1)/C and PdCo(3 : 1)/C as cathode catalysts at room temperature.

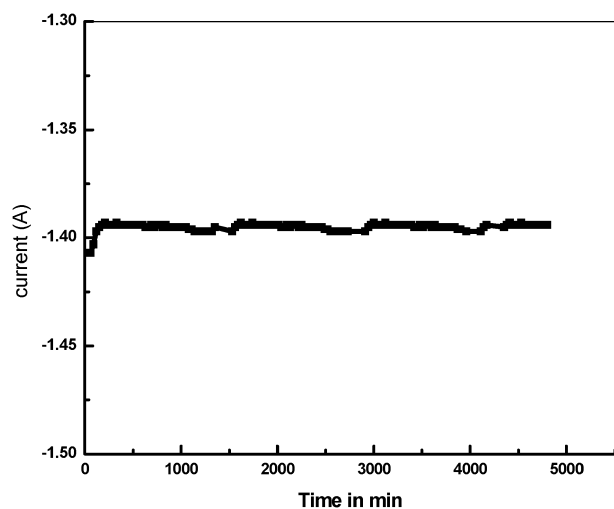


Fig. 10 Durability study for APEMFCs with PdCo(3 : 1)/C as the cathode catalyst at room temperature.

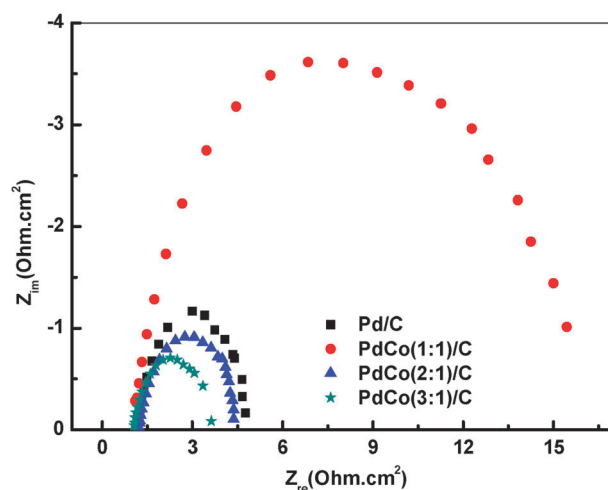


Fig. 11 Impedance spectra for APEMFCs comprising Pd, PdCo(1 : 1), PdCo(2 : 1), and PdCo(3 : 1)/C as cathode catalysts at the operating cell voltage of 0.8 V.

the direct correlation of ORR activity to charge transfer resistance is not consistent. But, in the present study, except the cathode catalyst, the other factors namely the catalyst loading, anode configuration, cell assembly, flow rate of reactant, pressure and operating conditions are identical and, hence, the variation in the charge-transfer resistance may be correlated to the cathode catalyst. The observed results are in conformity with the trend observed in polarization and ORR studies in regard to the catalytic activity.

3.6. ORR in an alkaline medium with methanol

Fig. 12 shows the cyclic voltammograms for methanol oxidation in deaerated aqueous solution containing 0.1 M KOH and 0.1 M methanol. Pd/C shows a large anodic current for methanol oxidation above -0.5 V vs. MMO while PdCo(3 : 1)/C, PdCo(2 : 1)/C and PdCo(1 : 1)/C alloys exhibit less activity for methanol oxidation. The addition of Co to Pd has reduced the activity of Pd for methanol oxidation. In other words, Pd alloy electrocatalysts have ORR selectivity in the presence of methanol.

Fig. 13 shows the linear sweep voltammograms on the Pd and Pd alloys in aqueous solution containing 0.1 M KOH and 0.1 M methanol under an oxygen atmosphere. Pd exhibited a large anodic (reversal) current above -0.15 V vs. MMO. The current reversal is due to methanol oxidation reaction. Among all the catalysts, PdCo(3 : 1)/C shows the least oxidation current due to methanol. The methanol oxidation caused the onset of cathodic limiting current to shift by ~ -200 mV. This result is due to the formation of a mixed potential which is caused by the simultaneous reaction of the methanol oxidation and oxygen reduction on the surface of the Pd electrocatalyst. Such a mixed potential at the cathode would negatively affect the cathode performance of the DMFCs.

3.7. X-ray photoelectron spectroscopy

Fig. 14(a) shows the XPS spectra for the Pd (3d) core level region for the PdCo(3 : 1)/C electrocatalyst. The binding energy separation between Pd 3d_{5/2} and 3d_{3/2} lines is 5.30 eV as reported in the literature.³⁶ De-convolution of the Pd 3d_{5/2}

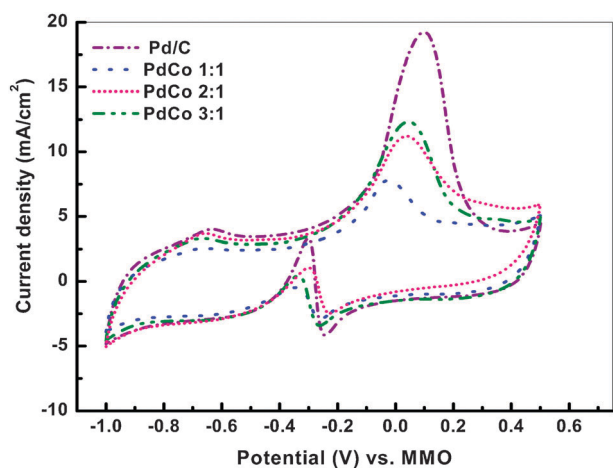


Fig. 12 Cyclic Voltammograms of Pd/C, PdCo(1 : 1)/C, PdCo(2 : 1)/C and PdCo(3 : 1)/C in deaerated solution containing 0.1 M KOH and 0.1 M CH₃OH with a sweep rate of 50 mV s⁻¹.

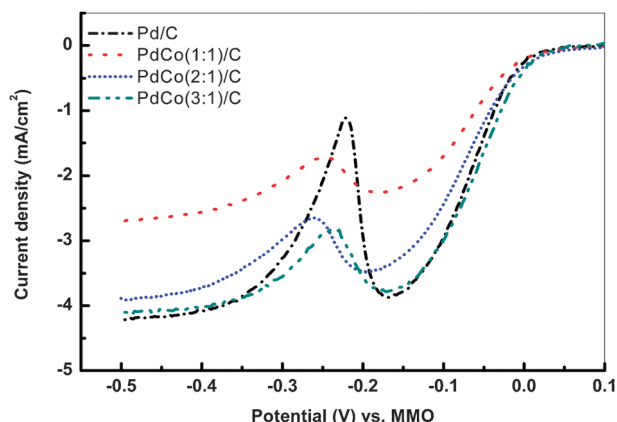


Fig. 13 Linear sweep voltammograms of Pd/C, PdCo(1 : 1)/C, PdCo(2 : 1)/C and PdCo(3 : 1)/C in oxygen saturated solution containing 0.1 M KOH and 0.1 M CH₃OH at 1600 rpm at a sweep rate of 3 mV s⁻¹.

signal has resulted in two doublets, which indicate the existence of at least two forms of Pd. From the literature, the binding energy of 335.2 eV corresponds to metallic Pd in Pd/C.³⁷ Here, the reported binding energy is associated with the Pd 3d_{5/2} core-level peak. In PdCo(3 : 1)/C, the Pd⁰ peak (Peak 1) shifted by 0.5 eV towards higher binding energy with respect to Pd/C. The peak 1 at the binding energy of 335.7 eV in the PdCo(3 : 1) electrocatalyst is in good agreement with the literature for the PdCo alloy.³⁷ This shift could be attributed to the chemical interaction between Pd and Co elements. In PdCo(3 : 1)/C catalyst, the binding energy originates from the d-band hybridization between Pd and Co upon alloying because the d-orbital forms stronger bonds between metal atoms, reducing the ability to form strong bonds with adsorbed reactants. The peak at 337.1 eV for PdCo (3 : 1)/C can be attributed to Pd²⁺ (peak 2) species.

Furthermore the binding energy shift indicates that the density of states (DOS) at the Fermi level decreases upon filling the d-band of Pd as electron density is transferred from Co to Pd atoms. As the d-band of Pd is filled by electrons

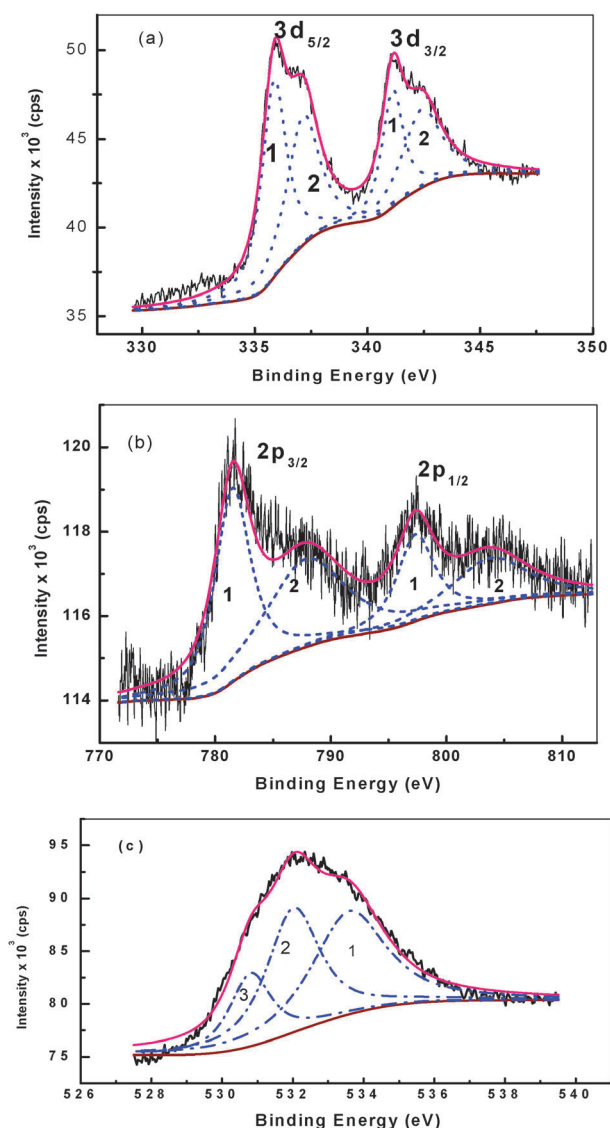


Fig. 14 (a) X-ray photoelectron spectra for the Pd (3d) region in PdCo(3 : 1)/C. Dotted line represents the fitted spectra. 1 and 2 correspond to the Pd⁰ and Pd²⁺ species, respectively, (b) X-ray photoelectron spectra for Co (2p) region in PdCo(3 : 1)/C and (c) X-ray photoelectron spectra for the O (1s) region in PdCo(3 : 1)/C.

donated by Co, the corresponding chemisorption of O₂, O/OH, O₂⁻, and H₂O₂ species on the electrode surface gets weakened, thus reducing their blocking effect in the O₂ reduction process. The DOS at the Fermi level affects the chemisorption of O and OH species on the surface and enhances ORR kinetics.³⁸

Fig. 14(b) shows the Co (2p) core level region for the PdCo(3 : 1)/C electrocatalyst. Two species of Co (2p_{3/2}) are present; one at 781.5 eV and the other one at 788.24 eV. The peak 1 at 781.5 eV is higher than the cobalt metallic (778.1–778.3 eV)³⁹ and it is in good agreement with the literature value for the PdCo alloy.⁴⁰ Fig. 14(c) shows the O (1s) core level region for the PdCo(3 : 1)/C electrocatalyst, three peaks are observed after deconvoluting the O (1s) spectra for the Pd/C. The peak at 530.8 eV is ascribed to O²⁻ in the PdO, the peak at 532.08 eV is due to adsorbed OH⁻ species, and the peak at 533.6 eV is due to physisorbed water.

3.8. First principles results

First principles calculations were performed to understand the catalytic properties of binary clusters. Initially, we studied the

structural stability of tetrahedral geometry of pure $\text{Pd}_n\text{Co}_{4-n}$ clusters, with $n = 0-4$. The optimized geometry, total magnetic moment, HOMO–LUMO gap and various bond distances of

Table 3 The optimized structure of O_2 adsorbed tetrahedral $\text{Pd}_n\text{Co}_{4-n}$ ($n = 1-4$) clusters, adsorption energy (E_{ads}), total spin moment (M), the HOMO–LUMO gap, and various bond lengths are given

Cluster	Geometry	E_{ads}/eV	M/μ_{B}	Gap/eV	Bond lengths/Å			
					O–O	Pd–Co	Pd–Pd	Co–Co
Pd_4		—	2	1.38	—	—	$2 \times 2.57, 2 \times 2.62, 2 \times 2.63$	—
Pd_3Co		—	3	1.00	—	2.37, 2.38, 2.36	2.74, 2.70, 2.68	—
Pd_2Co_2		—	4	0.28	—	$2 \times 2.47, 2 \times 2.46$	2.77	2.06
PdCo_3		—	7	0.23	—	2.41, 2.46, 2.50	—	2.40, 2.11, 2.26
Co_4		—	10	0.43	—	—	—	$4 \times 2.14, 2.75, 2.76$
$\text{O}_2@ \text{Pd}_4$		2.50	2	0.50	1.30	—	$2.46, 2 \times 2.68, 2 \times 2.70, 2.50$	—
		4.10	3	0.22	1.40	2.33, 2.46, 2.47	2.57, 2.67, 2.71	—
		3.80	5	0.00	1.31	2.42, 2.44, 2.45	$2 \times 2.62, 2.62, 2.63$	—
$\text{O}_2@ \text{Pd}_3\text{Co}$		3.53	3	0.40	1.36	2.49, 2.34	2.50, 2.75, 2.76	—
		2.90	1	0.56	1.30	2.35, 2.42, 2.44	2.65, 2.74, 2.75	—
		4.34	6	0.54	1.46	$2 \times 2.47, 2 \times 2.48$	2.57	2.25
$\text{O}_2@ \text{Pd}_2\text{Co}_2$		3.34	4	0.47	1.40	2.33, 2.37, 2.55, 2.61	2.71	2.15
		2.33	4	0.15	1.38	$2 \times 2.55, 2.62, 2.50$	2.50	2.03
		4.57	7	0.27	1.50	2.57, 2.40, 2.56	—	2.25
$\text{O}_2@ \text{PdCo}_3$		3.40	7	0.21	1.42	2.46, 2.44, 2.54	—	2.27, 2.16, 2.30
$\text{O}_2@ \text{Co}_4$		3.92	8	0.18	1.48	—	—	2.30, 2.25, 2.20

clusters are presented in Table 3. We observe that the total magnetic moment and average Pd–Pd bond distance decrease with increase in Co content, which is in agreement with XRD results. It infers that moment is mainly present in Co atoms. We also see that when three Co atoms are present in a cluster, the geometry of the cluster is significantly distorted due to non-uniform charge distribution among Co atoms. For example, three different Co–Co bond distances were observed in the optimized geometry of the PdCo₃ cluster and this tendency is also reflected in Pd–Co bond distances. Similarly, four shorter and two longer Co–Co bonds were observed in the optimized Co₄ cluster as shown in Table 3.

To gain insight of the experimental investigations namely that PdCo(3 : 1)/C shows better catalytic activity than the other binary clusters, such as PdCo(1 : 1)/C, PdCo(2 : 1)/C, and pure Pd clusters, an O₂ molecule is allowed to adsorb on the tetrahedral Pd₃Co cluster, with various orientations, adsorption energies are calculated and presented in Table 3. Our calculations predicted that the O₂ molecule prefers to bind side-on to Pd–Pd, Pd–Co and Co–Co atoms and the results are reported in Fig. 15. The energy of adsorption of the O₂ molecule on the cluster is 4.10 eV and this interaction energy helps to separate the O–O bond distance to 1.40 Å from its original distance of 1.24 Å. The configurations such as the O₂ molecule adsorbed end-on Pd or Co atoms and side-on Pd–Pd atoms are energetically less favorable. Similar calculations were carried out to study the O₂ adsorption on the other clusters, such as Pd₄, PdCo₃, Pd₂Co₂, and Co₄ clusters and results are given in Table 3. In all cases, O₂ prefers to bind side-on to Pd–Pd, Pd–Co or Co–Co atoms.

Fig. 15 shows the stable site of adsorption of an O₂ molecule. In general after adsorption of O₂ on Pd_nCo_{4–n} clusters, the O–O bond distance increases with increasing Co concentration. This bond distance increases from 1.30 Å in the Pd₄ cluster to 1.50 Å in the PdCo₃ cluster. On the other hand, the Co–O (~1.80 Å) and Pd–O (~2.04 Å) bond distances are quite invariant in all Pd_nCo_{4–n} clusters. As a result of increase in the O–O bond separation with Co concentration in binary clusters, the energy of adsorption of O₂ molecules on the cluster is also increased. However, in the case of the Co₄

cluster, this energy is decreased as compared with the other clusters. It is attributed to the increase in structural stability of the pure Co₄ cluster after adsorption of O₂. This is clearly observed from the four shorter and two longer Co–Co bond distances (2.14 Å and 2.75 Å, respectively) of the pure Co₄ cluster, which gets averaged into one set of Co–Co bond distances ranging from 2.20 to 2.30 Å after adsorption of the O₂ molecule on it. Similar tendency is also observed in the PdCo₃ cluster. Hence, our calculations revealed that the structural stability of the Co-rich binary cluster is increased after adsorption of the O₂ molecule.

Despite increasing the structural stability of Co rich binary clusters, we also noted that after adsorption of the O₂ molecule on the cluster, the Pd–Pd and Pd–Co bond distances are shortened, while the Co–Co bond distance is elongated. The origin of this variation in metal–metal bond distances is understood from the excess and depletion charge densities diagram given in Fig. 16. The charge densities of the O₂ molecule adsorbed at edge sites of two Co atoms and at edge sites of two Pd atoms of Pd₂Co₂ are given in Fig. 16. In fact, the d-orbitals involved in this charge transfer mechanism in the case of Pd and Co atoms are almost similar; however, the p-orbital of an oxygen atom is quite different. In the first case (Fig. 16(a)), where O₂ is bonded to a Co atom, the p-orbital is aligned along the Co–O bond, while the p-orbital is aligned perpendicular to Pd–O bond in the second case (Fig. 16(b)). Hence, it is concluded that the charge transfer mechanism between the O₂ molecule with Co and Pd atoms is quite different.

The optimum catalytic performance in binary Pd–Co clusters with 3 : 1 composition observed experimentally can be explained as follows. The O–O bond length of the adsorbed molecule for all the geometries is longer than that in the free molecule. The increased bond length is favorable for dissociation. It is well established that side-on adsorption of oxygen molecules on the catalyst is more favorable for ORR than end-on adsorption.⁴¹ Keeping this in view, the O–O bond distances for various geometries containing Pd and Co in varying ratios are compared. It is clearly seen from Table 3 that a maximum bond length is obtained for the Pd–Co bridge site in O₂@Pd₃Co, O₂@Pd₂Co₂ and the Co–Co bridge site in O₂@Pd₂Co₂. Adsorption energy for oxygen is found to be the maximum for O₂@Pd₃Co with oxygen adsorption on the Pd–Co bridge site and for O₂@Pd₂Co₂ with oxygen adsorption on the Co–Co bridge site. Dissociation of the oxygen molecule and formation of the O–H intermediate is favored on Pd–Co

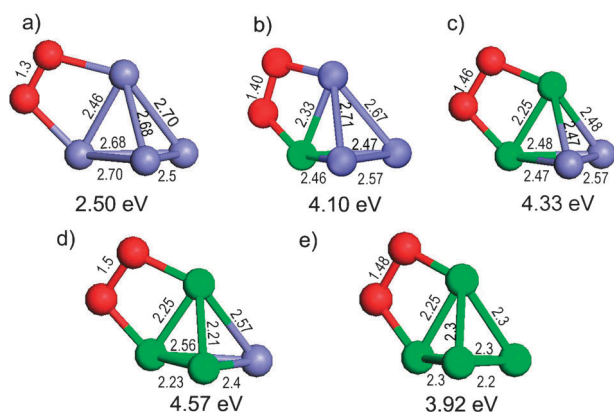


Fig. 15 The optimized geometry of stable configuration of O₂ adsorbed on Pd_nCo_{4–n} ($n = 0–4$) clusters with various bond distances and the adsorption energy. Pd, Co and O atoms are shown in purple, green and red, respectively.

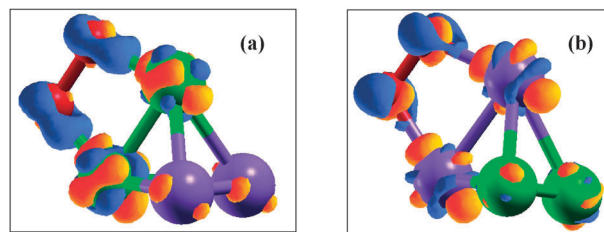


Fig. 16 The excess (blue coloured iso-surface) and depleted (orange) charge densities of O₂ (red) adsorbed at the edge site of (a) two Co (green) atoms and (b) two Pd (purple) atoms of Pd₂Co₂ clusters. The iso-surface is plotted for charge density of 0.1 ele Å^{–3}.

than on Pd–Pd.⁴¹ It is interesting to note that after adsorption of O₂ on these clusters, their HOMO–LUMO gap generally reduces. This decrease in the gap is due to a charge transfer between the cluster and the molecule. This gap is lower for O₂@Pd₃Co in comparison with O₂@Pd₂Co₂. Based on the above, it is concluded that the side-on dissociation of the oxygen molecule occurs on the Pd–Co bridge site in Pd₃Co, which is in agreement with the results obtained from half-cell and fuel cell studies.

4. Conclusions

APEMFCs comprising PdCo(3 : 1)/C as cathode catalyst show superior performance in relation to PdCo(2 : 1)/C, PdCo(1 : 1)/C and Pd/C, which is in agreement with the kinetic data obtained by half-cell studies. The ORR studies with methanol show that PdCo(3 : 1)/C has higher methanol tolerant behavior and better selectivity compared with other catalysts. The maximum electrocatalytic activity observed for PdCo(3 : 1) is explained by first principles calculations.

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