Solvothermal synthesis of Pt-Co/C cathode electrocatalyst for oxygen reduction reaction (ORR) in low temperature fuel cells

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Primarily, oxygen reduction reaction (ORR) kinetics at fuel cell cathode is slower on pure platinum due to its low activity in acidic medium. Owing to the excellent electrocatalytic property of Pt-Co/C nanoparticles for the oxygen reduction reactions (ORR) in fuel cell cathodes, a cubical phase face-centered cubic (FCC) Pt-Co/C electrocatalyst has been synthesized via solvothermal method using water as solvent. Various characterization techniques, such as X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Energy Dispersive X-ray spectroscopy (EDX) have been carried out for determining the crystallinity, surface morphology, particles size and elemental composition of Pt-Co/C electrocatalyst alloy, respectively. The XRD, EDX and TEM confirm the presence of well faceted FCC Pt-Co/C electrocatalyst with uniform distribution of these nano-size particles with atomic ratio of 3:1. The electrocatalytic activity of synthesized Pt-Co/C electrocatalyst for ORR was investigated by Cyclic Voltammetry (CV) test in acidic medium using HClO₄. Further, as CV stop crossing is increased, the activity of Pt-Co/C electrocatalyst increases due to less activation polarization with appreciable shifting of Pt-Co/C oxygen reduction peak potential towards more positive scale confirming better electrocatalytic property of the synthesized Pt-Co/C electrocatalyst for ORR.

Keywords: Solvothermal, Cathode reduction, Electrocatalyst, Fuel Cell, Water

It is seen in the recent past that the energy demand has gone up dramatically due to increased human population across the globe. Energy demand in the domestic and industrial sectors are met by conventional energy resources like, crude oil, coal, natural gas etc. Low temperature fuel cells could play better role to provide energy over existing conventional energy resources. However, the limited supply of conventional energy resources e.g., crude oil, coal and natural gas are the main reason to think over alternative energy producing devices like fuel cells. Fuel cell converts chemical energy of a fuel directly into electrical energy. Fuel cells are compact and silent. Nevertheless, fuel cell is a source of clean energy without emission of pollutants e.g., SOₓ and NOₓ etc. Fuel cells have attracted more attention due to their low degree of pollution and high theoretical efficiency. However, irrespective of fuel cell types, it suffers from different kind of losses/polarization like, activation polarization, ohmic polarization and concentration polarization. Activation polarization is due to the slow electrochemical reactions at the electrode surface, where the species are oxidized or reduced in a fuel cell electrode reaction. Activation polarization is directly related to the rate at which the fuel or the oxidant is oxidized or reduced. This loss in potential switch over the fuel cell reaction from reversible to irreversible, and it predominates during the start up of fuel cell. The origin of ohmic polarization comes from the resistance to the flow of ions in the electrolyte and flow of electrons through the electrodes and the external electrical circuit. The concentration losses occur over the entire range of current density. However, the concentration loss becomes prominent at high current density when it becomes difficult for fuel or oxidant to reach the fuel cell reaction sites due to the resistance to the mass transfer from outer surface (bulk) of gas diffusion layer (GDL) to electrocatalyst sites. Among these three types of major polarizations in fuel cells, activation polarization is the important one. As, literature suggest that faster electrode kinetics of fuel cell improves current density which in return gives high power density at low activation loss. Thus, fabrication of electrochemically active fuel cell electrode and its structure is an important aspect. The performance of electrode could be enhanced by synthesizing a suitable bimetallic alloy
electrocatalyst. It is seen in literature that the cathode activation loss is higher than the anode activation loss for low temperature fuel cell in acidic medium. Thus, developing an efficient cathode electrocatalyst could positively improve cell performance in terms of voltage and current density. Till date noble metal Pt based electrocatalyst is widely used at fuel cell voltage and current density. Till date noble metal Pt positively improve cell performance in terms of developing an efficient cathode electrocatalyst could for low temperature fuel cell in acidic medium. Thus, activation loss is higher than the anode activation loss electrocatalyst. It is seen in literature that the cathode ORR activity in the order of Pt > Pd > Ir > Rh 10. The electrocatalytic activity among other metals with the have predicted that Pt s hould have the highest (geometric effect) can strongly affect these energies 9. The binding energy of O\textsubscript{2} and OH on several metals have predicted that Pt should have the highest electrocatalytic activity among other metals with the ORR activity in the order of Pt > Pd > Ir > Rh\textsuperscript{10}. The activity of Pt metal enhanced, when Pt is alloyed with other transition metal that could be decode by change in electronic structure (the increased Pt d-band vacancy) and in Pt-Pt inter-atomic distance (geometric effect) can strongly affect these energies\textsuperscript{9}. The binding energy of O\textsubscript{2} and OH on several metals have predicted that Pt should have the highest electrocatalytic activity among other metals with the ORR activity in the order of Pt > Pd > Ir > Rh\textsuperscript{10}. The activity of Pt metal enhanced, when Pt is alloyed with other transition metal that could be decode by change in electronic structure (the increased Pt d-band vacancy) and in Pt-Pt inter-atomic distance (geometric effect). Alloying causes a lattice contraction, leading to a more favorable Pt-Pt distance for the dissociative adsorption of O\textsubscript{2}. Alloying with Pt produced a strong interaction between Pt metal-O\textsubscript{2} which weakens the O-O bonds\textsuperscript{9}. Thus, instead of pure Pt, we synthesized Pt-Co alloy on carbon support as ORR electrocatalyst, because pure Pt is very costly which would have been increase fuel cell fabrication cost. Solvothermal method was adopted to synthesize Pt-Co/C electrocatalyst as more material could be dissolved at higher temperature. Moreover, water as solvent provides many benefits e.g., with increase in temperature (i) ion product increases (ii) viscosity decreases (iii) polarity (dielectric constant) decreases, but increases with pressure\textsuperscript{11,12}. On the other hand, to make well-faceted nanocrystals, majority of the synthesis methods use strongly adsorbing molecules which are so-called capping agents to direct the reaction and crystal growth pathway to yield particles with the desired geometry\textsuperscript{13}. These capping agents remain strongly adsorbed on the particle surfaces even after the synthesis is complete. Thus, it must be removed if the nanoparticles are to be usable as electrocatalyst. Indeed, full removal of the capping agents without altering the nanoparticles structure is a challenging problem itself\textsuperscript{13}.

Now a day, many researches are being reported which focus on the improvement of the electrocatalytic performance of Pt-Co (alloy) catalyst for ORR\textsuperscript{14-16}. Yang et al. synthesized Pt\textsubscript{3}Co electrocatalyst of size 2-3 nm with Pt-enriched shells on a carbon support, which showed the improved catalytic performance towards ORR in comparison to commercial Pt/C catalyst\textsuperscript{17}. Zheng et al. synthesized porous Pt\textsubscript{3}Co nanoflowers via the co-reduction of Pt(acac)\textsubscript{2} and Co(acac)\textsubscript{3} in oleylamine. The alloyed Pt\textsubscript{3}Co nanoflowers displayed the enhanced electrocatalytic performance for ORR and in HClO\textsubscript{4}, compared with solid Pt\textsubscript{3}Co nanoparticles and commercial Pt black\textsuperscript{16}. Carpenter et al. developed well faced nanoparticles of Pt\textsubscript{3}Co without caping agent which have ORR specific activity 3-5 times greater than commercial pure Pt supported on carbon\textsuperscript{13}.

Till date no such paper on solvothermal synthesis of Pt-Co/C electrocatalyst using water as solvent has been reported. Moreover, only scanty literature is available on detail study of solvothermal synthesis of Pt-Co/C electrocatalyst and its through characterization. Thus, the aim of the present study is to synthesize highly active and well dispersed cathode electrocatalyst (Pt-Co/C) using solvothermal process without capping agents. In solvothermal synthesis pressure and temperature both play an important role for synthesizing nano-size Pt-Co/C electrocatalyst. However, selection of a suitable solvent, proper metal precursors and favorable thermodynamic conditions play significant role to synthesize electrocatalyst of exact composition and morphology. For reactions in aqueous phase, the solvent can control (i) the concentrations of chemical species in the solution affecting the kinetics of the reaction, and (ii) it also modifying the coordination of solvated species and induce specific structures\textsuperscript{11,12}. Thus, in this study, water was selected as a solvent for synthesis of Pt-Co/C electrocatalyst by co-reduction of platinum (II) 2, 4-pentanedionate and cobalt (II) 2, 4-pentanedionate precursor materials. Moreover, the manufacturing cost could be reduced using water as solvent due to it availability in nature in plenty amount. The synthesized catalysts were characterized using XRD, SEM, EDX, TEM analysis. The CV using a half cell in a three electrode cell assemble were also performed to investigate the electrocatalytic activity of synthesized Pt-Co/C electrocatalyst.
Experimental Section

Materials
Pt-Co/C electrocatalyst was synthesized by solvothermal reaction in Polytetrafluoroethylene (PTFE) lined vials mad of borosilicate glass. The metal precursors used to synthesized cathode electrocatalyst were acetylacetone compounds, platinum (II) 2, 4-pentanedionate (Alfa Aesar, USA), cobalt (III) 2, 4-pentanedionate (Alfa Aesar, USA). Activated carbon (Acetylene black, Alfa Aesar, USA) was used as support material for electrocatalyst and also to improve electronic conductivity at electrocatalyst layer of the prepared electrode. Distilled water was used as solvent. Toray carbon paper, TGP-H-60 (Alfa Aesar, USA) was used as substrate or gas diffusion layer for electrodecatalyst ink. A mixture of Nafion® and PTFE (60 % by wt, Sigma Aldrich, USA) were used as binder for electrode fabrication. Perchloric acid (HClO4) was used as electrolyte in CV analysis. Pure oxygen from cylinder was used as oxidant for ORR in CV experiment. Nitrogen from cylinder was used to maintain inert atmosphere in same CV experiment.

Synthesis of electrocatalyst
Initial reaction was carried out in glass vials with PTFE-lined cap. In solvothermal synthesis, platinum (II) 2, 4-pentanedionate (Alfa Aesar, USA), cobalt (III) 2, 4-pentanedionate (Alfa Aesar, USA) were dissolved in 12 mL of distilled water to yield concentrations of 30 mM platinum (II) 2, 4-pentanedionate and 10 mM cobalt (III) 2, 4-pentanedionate . The reaction mixture was heated at 150°C in PTFE-lined glass vials through heating oven for 4 h. The reaction mixture was heated at 150°C in PTFE-lined glass vials through heating oven for 4 h. The glass vials then removed from the heating oven and allowed to cool to ambient atmosphere before opening. The produced alloy precipitate mixture was sonicated with 10 mL ethyl alcohol in an ultrasonic water bath for 30 min and was then added to 15 mL of ethanol in which 160 mg of carbon had already been dispersed for 30 min using ultrasonic water bath at 30°C. The combined mixture was sonicated for another 30 min and then stirred for 2 h at 40°C. The solids were separated from the mixture by centrifugation, and the clear light yellow supernatant liquid was removed. The remaining traces of supernatant liquid and unwanted reaction products were removed from the solids with three wash cycle, one with 15 mL ethanol and two with 20 mL distilled water. The solids were removed from the final wash by filtration rather than centrifugation and were rinsed briefly with acetone and rinsed several times with distilled water. The prepared electrocatalyst was vacuum dried at a temperature of 80°C for 2 h and at 200°C for 24 h, respectively followed by collection of finished electrocatalyst.

Physical analysis of Pt-Co/C electrocatalyst
X-ray diffraction (XRD) analysis
X-ray diffraction (XRD) of electrocatalyst Pt-Co/C was performed on an 18 kW rotating anode XRD (RIGAKU, Japan). It generates high intensity X-rays with a wavelength of 1.54 Å (Cu-anode). Data were observed for the 20 ranges from 0° to 90°. The Phases were identified by comparing the observed data to reference data from International Center for Diffraction Data (ICDD) using Joint committee on powder diffraction standards (JCPDS 2003). Lattice parameters were calculated from the diffraction peak angle using Bragg’s Law. Crystallite size was estimated according to Scherrer’s equation.

Scanning electron microscope (SEM) analysis
The SEM images were collected using a scanning electron microscope (EVO-18 Research, Zeiss, Germany). Data for surface morphology of the electrode are visually observed at Extra High Tension (EHT) 20 kV, Work Distance (WD) of 8.5 mm and magnification of 10, 20 and 30 KX using tungsten filament.

Energy-dispersive X-ray (EDX) analysis
Energy-dispersive X-ray (EDX) spectroscopy analyzed the atomic ratios and elemental mapping of Pt-Co/C electrocatalyst. EDX technique coupled to a scanning electron microscope (Zeiss, Oxford Instruments, USA) with applying 20 kV using X-act 10 mm² silicon Drift Detector (SDD). EDX data were observed on standard C- CaCO3, O - SiO3, Co- Co and Pt - Pt, Jun-1999.

Transmission electron microscopy (TEM) analysis
Transmission Electron Microscopy (EFÍ™, Czech Republic) analyzed the particle size distribution and mean particle size. The mean particle size analyzed from TEM is verified by determining the particle size from XRD pattern using Scherrer’s formula. The tube voltage were maintained at 20 kV.

Electrochemical analysis of Pt-Co/C electrocatalyst
Fabrication of oxygen reduction reaction (ORR) cathode electrode
The cathode for low temperature fuel cell should be porous in nature to insure gas (oxygen from
cylinder) or air diffuse through its active zones. The cathode was prepared by dispersing the required quantity of Pt-Co (3:1 atomic ratio)/C, activated carbon and mixture of Nafion® ionomer and PTFE dispersion, which acted as binders. PTFE, along with pores at cathode, provide a flow network which allows easy escape of the reaction products from cathode. The cathode slurry was first prepared by dispersing the required quantity of activated carbon powder in Nafion® solution with a few drops of PTFE dispersion for 20 min using an ultrasonic water bath. The slurry was then uniformly spread on a carbon paper in the form of a continuous wet film using a brush to form solid porous cathode. It was then dried in an oven for 1 h at 80 °C. The dried cathode was sintered at 200°C for 2 h to obtain final form of the active electrode. The electrocatalyst (Pt-Co/C) loading at cathode electrode was maintained at 1 mg/cm².

**Half-cell studies**

Half-cell studies of cathode electrode were performed using cyclic voltammetry (PGSTAT 204, Autolab Netherland). The working cathode electrode was prepared from a long strip of GDL/ Toray Carbon Paper (Alfa Aesar, USA) whose one side tip was coated with electrocatalyst ink over a surface area of 1.35 cm x 0.4 cm. The other end of GDL/carbon paper strip was connected to the outside circuit of PGSTAT. The cathode was immersed in oxygen-saturated electrolyte (0.5 M HClO₄). In another experiment of 0.5 M HClO₄ solution was saturated with nitrogen gas to compare both CVs. Nitrogen or oxygen was supplied from the gas cylinder and purged through the HClO₄ solution using silicon tubing for 1 h. The terminals of the electrodes were connected to a Potentiostat-Galvanostat for cyclic voltammetry. The potentiostat was connected to a computer which recorded the current voltage data and NOVA 1.10 software was used to generate the voltammograms.

**Results and Discussion**

**X-ray diffraction (XRD) analysis**

The XRD patterns of synthesized Pt-Co/C electrocatalyst are shown in Fig. 1. The diffraction peak at 20 (theta) 25.36 is attributed due to support of carbon powder (Acetylene black). The XRD pattern shows the four main characteristics peaks of the face-centered cubic (FCC) structure of crystalline Pt, namely the planes (111), (200), (220) and (311) at corresponding 20 value 39.65, 45.85, 67.59 and 81.46 respectively. The XRD peaks of the Pt-Co/C electrocatalyst shifted to the higher 2θ angles of the Pt peaks which reveal the alloy formation between Pt and Co, due to incorporation of Co into the FCC structure of Pt metal. Super lattice reflections were observed in the XRD pattern of the Pt-Co/C catalyst indicating formation of ordered solid solutions. No peaks for Co (pure) or its oxides were observed, but their presence can not be discarded because they may be present in a small amount or in amorphous form. The lattice parameter of the Pt-Co/C alloy electrocatalyst at plane (111) is in agreement with the lattice constant for the bulk Pt-Co/C solid solution (0.393 nm). It indicates a high degree of metal alloying which contains no metal oxide species or the amount of metal oxide is negligible. The average size of the Pt and Pt-Co crystallites were estimated from the XRD (111) peak at 2θ, 39.65 using Scherrer’s equation and the measured size found to be 8.9 nm. This was validated by TEM result also.

![XRD pattern](image)

**Fig. 1 — XRD patterns of Pt-Co/C (3:1) electrocatalyst and Pt.**

**Scanning electron microscopy (SEM) analysis**

The surface morphologies of Pt-Co/C were observed in scanning electron microscope (SEM), as shown in Fig. 2a, (50.0 KX magnification) and Fig. 2b, (30.0 KX magnification). SEM images of electrocatalyst show that particles are of nano range (micro image) and its surface morphology indicate that spherical particles of Platinum-Cobalt were uniformly distributed. A very large white contrast could be seen in SEM images of Pt-Co/C, it may be because presence of Co metal particles in electrocatalyst which are charged by electron...
Energy dispersive X-ray (EDX) analysis

Energy dispersive X-ray (EDX) analysis was performed to analyze the presence of metal particles (Pt and Co) in synthesized electrocatalyst by solvothermal method using water as solvent. Figure 3, shows the EDX sequence of prepared electrocatalyst. It is clearly seen in the EDX that Pt, Co, and C are well distributed and present in the synthesized alloy Pt-Co/C electrocatalyst. The presence of oxygen was also observed and that has been reported by other investigator for Pt/C electrocatalyst.

Transmission electron microscopy (TEM) analysis

Figure 4a shows that the TEM of Pt-Co/C nanoparticles are spherical in the shape and uniformly distributed over carbon support (acetylene black). The carbon support as lighter particles are present in range of 30-50 nm size. The dark black dots uniformly distributed over the carbon support (lighter particles) are the Pt-Co catalyst particles. The particles size distribution of prepared Pt-Co/C electrocatalyst is shown in Fig. 4b, accordance to TEM image. The particle size of Pt-Co/C varies from 2 to 12 nm, with a mean diameter of 7.084 nm and standard deviation of 1.982 nm. Literature also suggests that size in the range of 3 nm shows excellent catalytic activity.

Cyclic Voltammetry of cathode electrode

Electrochemical reaction mechanism of oxygen reduction reaction (ORR) is quite complicated and involves many intermediates, primarily depending on the natures of the electrode material, catalyst and beam falling over it during SEM analysis (Fig. 2a and Fig. 2b).

Fig. 2 — SEM of Pt-Co/C (3:1) electrocatalyst (a) 50.0 KX magnification (b) 30.0 KX magnification.

Fig. 3 — EDX of Pt-Co/C (3:1) electrocatalyst
The oxygen reduction reaction in acidic medium is generally proceeds either by one step 4 electron (eq. (5)) or two step 2 + 2 electron pathway mechanism eqs. (2) and (4). The possible reaction mechanism of oxygen reduction at the cathode of PEMFC is as follows:

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\begin{align*}
O_2 + Pt & \rightarrow Pt-O_2 \quad \ldots (1) \\
Pt-O_2 + H^+ + 1e^- & \rightarrow Pt-HO_2 \quad \ldots (2) \\
Pt-HO_2 + Pt & \rightarrow Pt-OH + Pt-O \quad \ldots (3) \\
Pt-OH + Pt-O + 3H^+ + 3e^- & \rightarrow 2Pt + 2H_2O \quad \ldots (4) \\
or \quad O_2 + 4H^+ + 4e^- & \rightarrow H_2O \quad \ldots (5)
\end{align*}
\]

The electron transfer reaction and ORR depends upon different operating parameters and scan rate is one of them. It is well known that the electrochemical reaction can be manipulated through the scan rate. Figure 5, shows CV at different scan rate and its effect for the ORR on Pt-Co/C of 1 mg/cm² loading in oxygen saturated 0.5 M HClO₄. The oxygen reduction peaks were found in backwards scan of CV. The peak current density for forwards scan increases with the increase in scan rate. This electrode reaction is explained in reaction mechanism represented by equations (1-5), for the oxygen reduction reaction. The electron transfer reactions increases with increase in scan rate from 80 to 100 mV/s. The size of reduction peak in the reverse scan is explained in terms of amount of chemisorbed oxygen on the electrode surface. As the oxygen used by the reaction, a diffusion layer establishes. The size of the diffusion layer depends upon the voltage scan rate. In a slow scan rate, there will be enough time for diffusion layer to form a thicker layer than that for the fast scan rate. Thus, the oxygen flux to the electrode surface is considerably smaller at slow scan rate. It is clear in Fig. 5, that the CV at a scan rate of 100 mV/s produces two oxygen reduction peaks at peak potential of +1.32 V and +0.95 V respectively, compared with other scan rates due to less thicker
diffusion layer for transfer of electrons. Thus the scan rate 100 mV/s is taken as the basis in all the CVs to maintain consistency.

**CV with oxygen and nitrogen purged**

Figure 6a and 6b, show the CVs of ORR in an oxygen or nitrogen saturated electrolyte solution of 0.5 HClO₄ at a scan rate of 100 mV/s from -0.5 to +1.5 voltage span on Pt-Co/C cathode. The cathode electrode was made of carbon paper with loading of Pt-Co/C of 1 mg/cm² loading. The oxygen reduction current density peaks were observed in the backward scan at +0.95 and +1.32 V with current density of -0.048 mA/cm² and -0.260 mA/cm² for oxygen reduction reaction in Fig. 6a. This corresponds to 2 step 4 electrons pathway mechanism equations (1-4). The oxygen reduction peaks at +0.98 and +1.34 V indicates that the Pt-Co/C electrocatalyst has excellent ORR activity with negligible activation loss. The ORR peaks get disappeared in presence of saturated nitrogen electrolyte, as no oxidant is present at the surface of Pt-Co/C electrocatalyst (Fig. 6b)³³.

**Effect of electrolyte HClO₄ concentration**

Figure 7 shows the CV of oxygen reduction at a scan rate of 100 mV/s on a carbon cathode using 1 mg/cm² Pt-Co/C electrocatalyst loading. There are significant increase in peak current density and corresponding potential with the increase in electrolyte concentration from 0.25 M to 0.50 M HClO₄. The peak current density as changes from +0.544 to -0.260 mA/cm² when electrolyte concentration is increased from 0.25 M to 0.50 M due to more availability of H⁺ in electrolyte. The oxygen reduction potential shifts significantly towards a positive potential from +1.07 to +1.32 V for the changes of HClO₄ concentration from 0.25 M to 0.50 M HClO₄. This indicates that the activation overpotential is less for concentrated electrolyte solution (0.50 M HClO₄). Nevertheless, 0.5 M HClO₄ gives additional ORR peak at potential +0.95 V. This corresponds to 2 steps 4 electron mechanism with higher reaction rates which intern gives higher current density peaks. However, 0.25 M HClO₄ gives single peak for ORR. Thus, oxygen saturated 0.50 M HClO₄ electrolyte is taken as the basis in all the CVs to maintain consistency.

**Effect of stop crossing on CV**

Figure 8 shows the CV of oxygen reduction for oxygen saturated electrolyte solution of 0.5 HClO₄ at a scan rate of 100 mV/s for 3 stop crossing from voltage span -0.5 to +1.5 V. This test was performed to check the consistency in (2nd and 3rd cycle) activity of Pt-Co/C cathode during continuous imposing of charge on cathode. The 1st cycle/ 1st stop crossing shows two step four electron pathway mechanism (eq. 1-4), resulting peak current density of -0.048 mA/cm².

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Fig. 6 — Cyclic voltammetry for Pt-Co/C (3:1) electrocatalyst on high surface area carbon cathode at loading of 1 mg/cm² with 100 mV/s scan rate using (a) oxygen saturated (b) nitrogen saturated in 0.5M HClO₄ electrolyte.

Fig. 7 — Cyclic voltammetry for Pt-Co/C (3:1) electrocatalyst on high surface area carbon cathode at loading of 1 mg/cm² with 100 mV/s scan rate using oxygen saturated HClO₄ electrolyte of different concentrations.
and -0.260 mA/cm² at potential of 1.01 and 1.36 V respectively. It is evidence from Fig. 8, that continuous study of ORR on Pt-Co/C cathode gives interesting and improved result. As, the number of cycles of ORR increases, the no of oxygen reduction peaks get reduced which means kinetics is being shifted from 2 steps 4 electron mechanism to single step 4 electron mechanism. The single step ORR is more preferable than the two steps ORR mechanism. The peak potential also get shifted to more positive direction for 2nd (at +1.43 V) and 3rd (+1.45 V) which are better than of 1st cycle (at 1.36 V). This trend may be due to slowness of the reaction at the beginning (1st cycle), high activation overpotential loss. On the other side oxygen reduction peak in 2nd cycle and 3rd cycle get shifted in more positive voltage direction in composition to 1st oxygen reduction peak. It implies that after 1st cycle, electrocatalyst sites become more active. Thus, it gives reaction path with low activation overpotential. However, the peak current density obtained from 2nd and 3rd cycle is +0.116 and +0.294 mA/cm², respectively. Which are lower than 1st cycle reduction peak current density of -0.260 mA/cm². It may be because of gradually decrease in dissolve oxygen concentration in electrolyte.

**Conclusion**

The solvothermal synthesis of Pt-Co/C (3:1) electrocatalyst alloys for oxygen reduction reaction (ORR) using water as solvent showed excellent performance. Proper faced nanoparticle (sub-12 nm) Pt-Co/C electrocatalyst was synthesized without capping agent and has uniform distribution of Pt-Co on carbon support. The physical and electrochemical characterization proves that the synthesized electrocatalyst Pt-Co/C alloys is better than the electrocatalyst reported in the open literature till date. The ORR on Pt-Co/C in followed by the two step four electron mechanism. However, prolonged use of Pt-Co/C reduces activation overpotential which resulting in single step four electron mechanism. This is very interesting and significant observation which have never been reported earlier. The ORR peak potential at more positive indicates, Pt-Co/C to be the better oxygen reduction cathode for low temperature fuel cell applications.

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