The Beneficial Role of the Cometals Pd and Au in the Carbon-Supported PtPdAu Catalyst Toward Promoting Ethanol Oxidation Kinetics in Alkaline Fuel Cells: Temperature Effect and Reaction Mechanism

Jayati Datta,† Abhijit Dutta,‡ and Sanjeev Mukherjee‡

†Electrochemistry & Fuel Cell Laboratory, Department of Chemistry, Bengal Engineering and Science University, Shibpur, Howrah—711 103, West Bengal, India
‡Department of Chemistry and Chemical Biology, 317 Egan Center, Northeastern University, 360 Huntington Avenue, Boston, Massachusetts 02115, United States

Supporting Information

ABSTRACT: Electrochemical investigations have been carried out to study the oxidation kinetics of ethanol in alkaline solution on carbon-supported ternary alloy catalysts Pt−Pd−Au within the temperature range of 20–80 °C. To derive a better understanding of the contribution of each of the metallic components toward the catalytic oxidation of ethanol, some of the investigations were extended to the individual noble metals for comparison, however, at a single temperature (20 °C). The individual metals could barely show their catalytic efficiency toward ethanol oxidations when compared to the alloyed catalyst. The ternary catalyst exhibited much lower values and a larger temperature dependence of onset potential for ethanol oxidation. With the rise of potential, the apparent activation energy (Ea(app)) for ethanol oxidation on the Pt/C electrode increased, whereas a decreasing trend was observed with the Pt30Pd38Au32/C electrode. It was suggested that the Pt30Pd38Au32/C electrode bears an excellent tolerance toward ethanolic residues, for the temperature range studied. In correlation with the results obtained from the above study, attempts were made to elucidate the oxidation reaction mechanism, and this further evoked interest in extending the work to the estimation of products formed during oxidation of ethanol within the same temperature range through ion chromatographic analysis. The pronounced increase in the quantity of oxidation products, such as acetate and carbonate, obtained over the ternary catalyst as compared to single Pt, substantiates the kinetic enhancement of ethanol oxidation, attributable to the cometal partnership between Pd and Au when incorporated in the Pt matrix. In summary, the multimetallic nanocrystallites can not only show their capability of extracting the best possible number of electrons from the alcohol fuel in alkaline solutions, harnessing more energy, but also, at the same time, bring down the cost of the catalyst material by reducing the Pt content to a considerable extent.

1. INTRODUCTION

The Pt-based alloys and composites are being explored as the alternatives to single Pt for electrocatalysis in fuel cell reactions.1−8 Particularly for the anodic reaction in DEFCs operating in acidic environments, several Pt-based alloys have superseded the single Pt with respect to their catalytic activity toward promoting faster kinetics and complete conversion of the alcohol fuel to the end products. The success in electrocatalysis of these alloy materials has been attributed to the bifunctional mechanism9 and the electronic effect10−12 induced by the electronic interaction of Pt with other metals. However, the search for efficient catalysts for selective oxidation in alkaline solutions is scarce. Therefore, a major thrust may be put to investigate the catalytic activity of the alloy materials in alkaline media for obtaining favorable kinetics and better selectivity toward CO2 production.13−16

In the present investigation, the carbon-supported single metal catalysts, Pt/C, Au/C, and Pd/C, and the ternary Pt:Pd:Au/C [∼1:1:1] catalysts were synthesized through a borohydride reduction method. The identification of crystal phases, the matrix morphology, and the surface area of the nanoparticles have been studied by X-ray diffraction (XRD), transmission electron microscopy (TEM-EDAX), and the Brunauer–Emmet–Teller (BET) method, respectively. The catalytic activity toward ethanol oxidation in alkaline solutions was investigated with the help of several electrochemical techniques, such as cyclic voltammetry (CV), chronomperometry (CA), and electrochemical impedance spectroscopy (EIS), and the temperature effect on ethanol oxidation was investigated with Pt/C and PtPdAu/C electrodes in particular. Apparent activation energies (Ea(app)) for the oxidation reaction were determined at different potentials

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Table 1. Results of EDAX, XRD and Voltammetric Analysis of the Single and Ternary Catalysts

<table>
<thead>
<tr>
<th>electrocatalysts</th>
<th>Pt/Pd/Au (atomic ratio)</th>
<th>EDAX composition (at. %)</th>
<th>interplanar distance (Å)</th>
<th>lattice parameter (Å)</th>
<th>average crystallite size (nm)</th>
<th>ECSA (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>1:0:0</td>
<td>Pt: 100</td>
<td>2.260</td>
<td>3.925</td>
<td>3.84</td>
<td>27.3</td>
</tr>
<tr>
<td>Pd/C</td>
<td>0:1:0</td>
<td>Pd: 100</td>
<td>2.231</td>
<td>3.893</td>
<td>3.40</td>
<td>19.8</td>
</tr>
<tr>
<td>Au/C</td>
<td>0:0:1</td>
<td>Au: 100</td>
<td>2.240</td>
<td>4.081</td>
<td>3.22</td>
<td>11.3</td>
</tr>
<tr>
<td>PtPdAu/C</td>
<td>1:1:1</td>
<td>Pt: 30</td>
<td>2.165</td>
<td>3.903</td>
<td>3.90</td>
<td>69.3</td>
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<tr>
<td></td>
<td></td>
<td>Pd: 38</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Au: 32</td>
<td></td>
<td></td>
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</tr>
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</table>

within the temperature range of 20—80 °C. The reaction products were also estimated through ion-chromatographic analyses within the same temperature regime. On the basis of the information obtained, the kinetics and mechanism of the reaction were elucidated.

2. EXPERIMENTAL SECTION

2.1. Preparation of Catalysts. The nanocatalysts (40 wt % each) of the single metals, Pt, Au, and Pd, and the ternary system PtPdAu/C were prepared under the NaBH₄-reduction scheme from the chemical bath containing the corresponding precursor salts (H₂PtCl₆, PdCl₂, AuCl₄), Arora Matthey Ltd. and their mixtures in 0.002 M concentrations of each of the salts. An appropriate amount of Vulcan XC-72 carbon (Cabot India) was added to the 400 mL of milli-Q water (ρ = 18.2 MΩ·cm), and the mixture was ultrasonicated for 30 min, followed by stirring for 1 h. Subsequently, an excess quantity of 0.05 M NaBH₄ (Merck) solution was added, drop by drop, to the mixture with vigorous stirring until the yellowish-brown colloidal solution became colorless, containing dispersed black metal particles for the complete reduction of metals from the precursor salt. The resulting heterogeneous colloidal mixtures were allowed to stir for 1 h at room temperature and centrifuged. Black metal catalyst particles were then isolated by centrifugation, and the supernatant colorless liquid was tested by silver nitrate to detect the presence of any residual bromide or chloride ion in solution. The catalysts were washed with plenty of milli-Q water, and the bromide test was done until the yellowish-brown colloidal solution became colorless. For the complete reduction of metals from the precursor salt. The recorded XRD patterns of the supported catalysts were determined by using the powder XRD technique. The data were determined by using the Seifert 2000 diffractometer operating with CuKα radiation (λ = 0.1540 nm) generated at 35 kV and 30 mA. Scans were recorded at 1° min⁻¹ for 2θ values between 2 and 90°. Scherrer and Bragg formulas were employed to calculate the mean diameter and the lattice parameter of the catalysts. The recorded XRD patterns were analyzed following the JCPDS file. To get the morphology and particle size, TEM images of catalysts were obtained by using an FEI model STWIN operated at an accelerating voltage of 200 kV. Specimens for TEM analysis were prepared by ultrasonically suspending the particles in alcohol. A drop of the suspension was deposited onto a standard carbon-coated Cu grid and allowed to dry before being inserted into the microscope. The particle size distribution histograms were obtained by the observation of about 300 particles from the four different locations of the corresponding TEM images. An electron-dispersive X-ray detecting system, EDAX, coupled with the TEM instrument, was used to analyze the chemical composition of the alloy, considering several regions of the catalyst particles throughout the surface. The spatial resolution of the EDAX probe is 0.35 nm. The adsorption isotherm of the catalysts was recorded at 77 K by the BET method using nitrogen as the adsorbate in a Quantachrome Autosorb instrument (model AS1-CT). Prior to the measurements, samples were degassed at 150 °C for 30 min. The surface area was evaluated according to the BET theory, using the multipoint method at relative pressures up to P/P₀ = 0.2, and the total volume (V₅₆) was calculated from the volume of nitrogen adsorbed at near to saturation pressure, P/P₀ = 0.99. The volume of micropores (Vₚ) was derived from the so-called t-plot dependence of the nitrogen sorption isotherm. The pore size distribution was derived from the adsorption isotherm according to Barrett–Joyner–Halenda (BJH) model calculations.

2.2. Surface Characterization and Morphology of the Catalyst Matrix. The characteristics of the crystalline structure of the supported catalysts were determined by using the powder XRD technique. The data were determined by using the Seifert 2000 diffractometer operating with CuKα radiation (λ = 0.1540 nm) generated at 35 kV and 30 mA. Scans were recorded at 1° min⁻¹ for 2θ values between 2 and 90°. Scherrer and Bragg formulas were employed to calculate the mean diameter and the lattice parameter of the catalysts. The recorded XRD patterns were analyzed following the JCPDS file. To get the morphology and particle size, TEM images of catalysts were obtained by using an FEI model STWIN operated at an accelerating voltage of 200 kV. Specimens for TEM analysis were prepared by ultrasonically suspending the particles in alcohol. A drop of the suspension was deposited onto a standard carbon-coated Cu grid and allowed to dry before being inserted into the microscope. The particle size distribution histograms were obtained by the observation of about 300 particles from the four different locations of the corresponding TEM images. An electron-dispersive X-ray detecting system, EDAX, coupled with the TEM instrument, was used to analyze the chemical composition of the alloy, considering several regions of the catalyst particles throughout the surface. The spatial resolution of the EDAX probe is 0.35 nm. The adsorption isotherm of the catalysts was recorded at 77 K by the BET method using nitrogen as the adsorbate in a Quantachrome Autosorb instrument (model AS1-CT). Prior to the measurements, samples were degassed at 150 °C for 30 min. The surface area was evaluated according to the BET theory, using the multipoint method at relative pressures up to P/P₀ = 0.2, and the total volume (V₅₆) was calculated from the volume of nitrogen adsorbed at near to saturation pressure, P/P₀ = 0.99. The volume of micropores (Vₚ) was derived from the so-called t-plot dependence of the nitrogen sorption isotherm. The pore size distribution was derived from the adsorption isotherm according to Barrett–Joyner–Halenda (BJH) model calculations.

2.3. Fabrication of the Electrodes. A catalyst ink was prepared by taking an appropriate amount of catalyst in 5 wt % Nafion ionomer (Electrochem. Inc., USA) and 2-propanol (GR grade, Merck), and the mixture was sonicated. A calculated amount of this slurry was micropipetted out onto the graphite support (0.65 cm²) to maintain a constant catalyst loading of 0.77 mg cm⁻². A graphite plate (GLM grade, Graphite India Ltd.) with a thickness of approximately 2 mm was used as the support for the working electrode.

2.4. Electrochemical Measurements. Electrochemical measurements were conducted using a computer-controlled potentiostat/galvanostat with PG stat 30 and FRA modules (Eco Chemie B.V., The Netherlands). Ethanol (AR grade, Merck) was added to the nitrogen (XL grade, 99.999%, BOC India Ltd.) saturated 0.5 M NaOH electrolyte to make a 1.0 M EtOH concentration. All these solutions were prepared using Mili-Q water. The geometrical area of the electrocatalyst exposed to the solution was always 0.65 cm². Voltammetry was carried out in a glass cell using a conventional three-electrode setup incorporating a mercury/mercurioxide (Hg/HgO) reference electrode and a bright Pt foil (10 mm × 10 mm) counter electrode along with the working electrode fabricated with the synthesized catalysts. Steady-state potentiostatic data were recorded after polarization for 5 min. Electrochemical impedance measurements were performed with an amplitude of 5 mV in the frequency range of 30 kHz to 30 mHz at a potential of −0.3 V.

2.5. Ion-Chromatographic Analysis. Aliquots from the working electrolyte were analyzed by ion chromatography after polarization at constant potential for 2 h at selected temperatures in the range of 20—80 °C. Metrohm’s Advanced Modular Ion Chromatography systems, a Metrosep A Supp 5-250 column and...
a Metrosep A Supp 4-550 organic acid column, were used for analyzing the acetate and carbonate ions. A 1 mL sample solution was diluted with 19 mL of filtered Milli-Q water, and 25 μL of this sample was injected into the ion chromatograph.

3. RESULT AND DISCUSSION

3.1. Morphology and Structural Characterization of PtPdAu/C Electrocatalyst. It has been found in an earlier work that optimization of the catalyst loading with respect to the carbon content in the catalyst matrix, for a fuel cell reaction, is an essential prerequisite to deriving the best catalytic performance of the nanoparticles toward the respective red-ox processes (see Figures S1−S3 in the Supporting Information). In this regard, a 40% catalyst loading was found to be the choice for catalyst support combination.

The EDS measurement was recorded to derive the atomic composition of the PtPdAu/C catalysts prepared from the chemical bath containing the metal precursors, all having a equimolar concentration, and the corresponding atomic ratios are given in Table 1.

The XRD patterns in Figure 1 clearly demonstrate that the Pt/C, Pd/C, Au/C, and Pt30Pd38Au32/C alloy catalysts have face-centered cubic (fcc) structures. All the catalysts exhibited diffraction peaks of (111), (200), (220), (311), and (222) planes corresponding to an fcc crystal structure (JCPDS 04-0802). The 2θ values of the (111) planes were found to be shifted slightly from the values of Pt/C at 39.763 ± 0.004 for Pd/C, 38.184 for Au/C, and 40.069 for the ternary system PtPdAu. Assuming alloy formation among Pt, Pd, and Au based on a substantial solid solution, such a shift can be attributed to the difference in atomic sizes of the order of Pd > Pt > Au. Seemingly, the gold catalyst exhibited the lowest 2θ value, being significantly different from that of the other catalysts. The lattice parameters of these catalysts were obtained from the XRD patterns displayed in Table 1. It was found that the addition of Pd and Au to the Pt matrix barely makes any effect on the crystalline structure of Pt/C because Pt, Pd, and Au have almost the same fcc crystalline
structure. The diffraction position of the ternary catalyst is positively shifted compared with that of the other catalysts, resulting in the decreased lattice parameter of 0.3903 for Pt30Pd38Au32/C compared with 0.3925 nm of pure Pt/C.

Low-resolution TEM images of Pt30Pd38Au32/C catalysts and the corresponding particle size distribution histograms are shown in Figure 2a,b, respectively, and the data from TEM analysis are listed in Table 1. There is a clear tradeoff in particle size with the incorporation of Au in the ternary system. The average sizes of the particles for all the catalysts calculated by using the Debye–Scherrer equation, agreed well with the TEM results, and the size distribution is found to be narrower with almost 80% of the catalyst particles in the 3–5 nm range. The fringe patterns for the Pt30Pd38Au32/C catalyst are shown in Figure 2c, where the crystalline plane is calculated with the help of FFT analysis (Figure 2c, inset). The d-spacing of Pt30Pd38Au32/C is shifted to 0.2165 nm from 0.226 nm, the normal value of Pt (111) (JCPDS 04-0802), indicating alloy formation, which is also supported by XRD data, discussed earlier. The overall impression is such that the narrow size distribution and better dispersion are achieved due to the existence of Au in the ternary matrix. A representative point-resolved EDS spectrum (Figure 2d) collected from a number of individual particles reveals that the ternary catalyst matrix is grown with an ensemble of atoms of the individual metals Pt, Pd, and Au forming the nanoparticles.

A typical reversible curve representative of a type III nitrogen adsorption and desorption isotherm and the Vulcan XC-72 [C(V72)] carbon reversible curve representative of a type IV/III are exhibited in Figure 3a. The single and ternary catalysts were studied according to the Brunauer–Deming–Deming–Teller (BDDT) classification, and the types of hysteresis were attributed to cylindrical pores. Pore volume and pore size distributions (PSDs) were calculated on the basis of the BJH model performed from the adsorption branch of the isotherm, as shown in the inset of Figure 3a.

The adsorption isotherms associated with the structure of the single and ternary catalysts are essentially those of the combination of micropores and mesopores and as further clarified from the pore size distribution (PSD) curves. Small micropores (<2 nm) in the carbon-supported catalyst decreases the catalyst utilization because the mass transport of reactants and products become insignificant for these tiny micropores. When the macropore size is larger than 50 nm, the surface area becomes smaller and the electrical resistance increases.21 Ternary catalysts on Vulcan XC 72 with optimum pore sizes in the range of 2–50 nm (as shown in Figure 3a, inset) become useful as they can render a better ability to enhance both the dispersion and the utilization of metals in this range. The relevant structural parameters of all the catalysts determined on the basis of the isotherms18 are revealed in Figure 3b, where it is observed that, with the incorporation of Pd and Au into the Pt matrix, the total BET surface area increases along with the external surface area and the micropore area of the catalyst surface. This indicates that Pt30Pd38Au32/C catalysts not only intercalate into the micropore of the graphite support but also are grown on the external surface area of the support. The large quantity of micropores can enhance the adsorbility of the catalyst and extend the active sites. On the other hand, higher surface areas and larger pore volumes allow a higher degree of catalyst dispersion as well as lead to highly integrated interconnected pore systems with periodic order and thus enable better utilization of catalyst particles by efficient transport of reactants and products through the catalyst matrix.

![Figure 3](image-url)

Figure 3. (a) Nitrogen adsorption (filled) and desorption (unfilled) isotherms for single and ternary catalysts. Inset: pore size distributions calculated from the nitrogen adsorption–desorption isotherms. (b) Different surface areas for Pt/C, Pd/C, Au/C, and Pt30Pd38Au32/C.

![Figure 4](image-url)

Figure 4. Cyclic voltammograms of Pt/C, Pd/C, Au/C, and Pt30Pd38Au32/C in 0.5 M NaOH. Scan rate = 50 mV s⁻¹. Inset: magnified view of the oxide reduction peak region and the hydrogen adsorption–desorption region.

3.2. Electrochemical Investigation and the Temperature Effect on the Electrode Kinetics. Typical voltammograms of Pt, Pd, Au, and PtPdAu catalysts in 0.5 M NaOH are shown in Figure 4. The well-established features of hydrogen adsorption and desorption, double layer charging, oxide formation, and oxide reduction are evident from the voltammograms of all the
catalysts studied. A measure of the real electrochemical surface area $A_e$ (cm$^2$ Pt) can be obtained from the voltammogram using the following equation

$$A_e = \frac{Q_h}{Q_m}$$

where $Q_h$ is the saturated hydrogen coverage on the electrode ($\mu$C) and $Q_m$ is the charge associated with monolayer adsorption of hydrogen ($\mu$C cm$^{-2}$ Pt). It is assumed that each surface platinum atom is associated with one chemisorbed hydrogen atom, allowing the charge corresponding to the area under the hydrogen adsorption peaks, $Q_m$, to be converted to the real electrochemical surface area. The charge associated with a monolayer of hydrogen is commonly taken as 210 $\mu$C cm$^{-2}$ for Pt$^{22,23}$ after double layer correction. However, for Pd-containing catalysts, the method based on the hydrogen adsorption charge seems to be less reliable because Pd can absorb large quantities of hydrogen (up to 900 times its own volume). The real ECSA of the Pd-containing PtPdAu/C catalyst is determined by considering the Columbic charges corresponding to the oxide reduction peak of the alloyed catalyst. However, it is not possible to measure the ECSA value accurately by using this method because the reduction peaks may be ascribed to the reduction of the oxides of Pd, Pt, and Au formed on the surface of the PtPdAu/C catalyst during the positive scan.$^{24}$ The charges required for the reduction of PdO (qPdO-red), PtO (qPtO-red), and Au$_2$O$_3$ (qAu$_2$O$_3$-red) monolayers were taken to be 405, 420, and 400 $\mu$C cm$^{-2}$, respectively, as reported in the literature.$^{25-27}$ The mean value of charges required for the oxide reduction of the alloyed catalyst with the atomic composition of Pt$_{30}$Pd$_{38}$Au$_{32}$ was calculated to be 409.1 $\mu$C cm$^{-2}$ and used for evaluating the ECSA of the alloyed catalyst, summarized in Table 1. The value of ECSA for Pt$_{30}$Pd$_{38}$Au$_{32}$/C was found to be far higher than the value obtained for pure metal catalysts, reflecting the higher catalytic surface area for the ternary alloyed catalyst.

The oxidation of Pt$_{30}$Pd$_{38}$Au$_{32}$/C surfaces commences at a more negative potential than those observed for other catalysts, and the double layer charging region and beyond is far more exuberated, indicating dipolar interactions, followed by oxide formation, in this region.

With the incorporation of Pd and Au into the Pt matrix, the oxidation current rises in the potential region of $-750$ to $+250$ mV, as shown in Figure 5, almost 4 times that of Pt and in the order of PtPdAu > Pd > Pt > Au.

The forward peak current in the anodic sweep and the reversed peak current in the cathodic sweep are compared in Figure 6, and a significant increase in both the current densities are observed with the ternary catalyst compared with the single metals. Thus, the possibility of using the single metal as an effective catalyst for ethanol oxidation becomes less important. Hence, for the rest of the investigations involving the reaction kinetics at different temperatures, the studies on Au and Pd were abandoned and the results of electrode kinetics were compared for the ternary catalyst and the single Pt only.

Figure 7a,b represents the cyclic voltammograms for the EOR on Pt/C and Pt$_{30}$Pd$_{38}$Au$_{32}$/C in 0.5 M NaOH containing 1.0 M ethanol at the temperatures of 20, 40, 60, and 80 °C. The Pt/C and Pt$_{30}$Pd$_{38}$Au$_{32}$/C catalysts show significantly different CV profiles, particularly at higher temperatures. The ethanol oxidation peak current densities obtained with Pt/C in the forward sweep were raised by a factor of 3 as the temperature increased from 20 to 80 °C (shown in Figure 7a), whereas the negative going sweeps display a sharp vertical increase of the reverse oxidation peak, which are more prominent at higher temperatures. This sharp rise in current on Pt/C is indicative of the fact that the ethanolic residues remaining unoxidized on the surface during the forward sweep can only be oxidized by the Pt oxide formed at higher potentials. As the temperature was increased, the potential differences between forward and reverse peaks were reduced, suggesting that surface activation of Pt/C by OH species is facilitated at higher temperatures. The influence of temperature on Pt$_{30}$Pd$_{38}$Au$_{32}$/C toward the ethanol oxidation is far more significant. Considering the voltammograms of the ternary system, as shown in Figure 7b obtained in the same temperature range, the oxidation peak current densities was found to increase by almost 4 times, when the temperature was increased from 20° to 80 °C. In contrast to the Pt catalyst, the diminution in the reverse oxidation current with the ternary system is noted and a considerable rise in anodic peak intensity is observed, particularly at high temperature. This points toward a fair catalytic performance of the Pt$_{30}$Pd$_{38}$Au$_{32}$/C system compared to other catalysts.
Pt/C clearly demonstrates that the catalytic activity of the former is improved to a reasonable extent with a moderate increase in temperature. Thus, it is suggested that the catalytic activity of the former is improved to a reasonable extent with a moderate increase in temperature. 

The pronounced influence of temperature on the electrocatalysis of the ternary system as compared to Pt alone is further clarified with the variation of $i_\text{p}$ with temperature, as shown in Figure 8a. For the Pt/C catalyst, the anodic peak current ($i_\text{p}$) is practically invariant with temperature, whereas a substantial increase in anodic peak current is observed for the Pt30Pd38Au32/C catalyst. A considerable negative shift of the onset ($E_{\text{onset}}$) potential was observed in the alloyed electrodes, as shown in Figure 8b. A constant slope of $-3.10 \text{ mV/°C}$ for the Pt30Pd38Au32/C catalyst as compared with $-0.4 \text{ mV/°C}$ for Pt/C clearly demonstrates that the catalytic activity of the former is improved to a reasonable extent with a moderate increase in temperature. Thus, it is suggested that the effect of introducing Au into Pt or PtPd may cause a monotonic decrease of reduction potential and thereby increase the tendency of surface oxide formation.

Figure 9a shows chronoamperometric experiments in 0.5 M NaOH containing 1.0 M ethanol on Pt/C and Pt30Pd38Au32/C at different temperatures to determine the stability of the catalysts. A decrease of current density was recorded at the beginning of each experiment for both Pt/C and Pt30Pd38Au32/C catalysts at each temperature. The Pt/C electrode showed rapid current decay and very low initial and final current densities for all the temperatures. This indicates that the Pt/C surface is prone to poisoning by ethanolic residues. For Pt30Pd38Au32/C catalysts, current decay was comparatively low and reasonably high initial as well as final current densities were observed. Thus, Pt30Pd38Au32/C catalysts conform to a greater tolerance to poisoning species (COads) on the Pt group of metals. However, in the present case, it appears that the reaction in its course does not follow the same pathway for the Pt catalyst and the ternary alloy. The above observations were further clarified by the negative deviations from Cottrell’s law ($i \propto t^{-1/2}$) due to blocking of the surface area in contrast to the normal positive deviations as a result of unwanted stirring of the solution.

Moreover, a modification of that equation, which is known as Anson’s plot ($Q \propto t^{1/2}$), allows the determination of the amount of charge involved in the process for the different catalysts under investigation. Here, we have taken the advantage of applying chronocoulometry (CC) (the study of species adsorbed to the surface of the working electrode) over chronoamperometry (CA), and it is possible to separate the charge due to the electrolysis of the adsorbed molecules from the charge due to the electrolysis of molecules in solution and the double layer charge. Figure 9c demonstrates the high level of charge on the ternary electrodes, even at 40 °C, which is much higher than that produced by Pt at 80 °C. This is better understood when we followed the Arrhenius plots to derive the activation energy of the reaction over the temperature range with Pt and Pt30Pd38Au32/C catalysts.

Figure 10a shows Arrhenius plots for ethanol oxidation on the Pt/C and Pt30Pd38Au32/C catalysts at different potentials. Linear

\[
\delta = \frac{100}{t_0} \times \frac{\text{d}i}{\text{d}t}_{t > 500 \text{s}} \quad \text{% per s}
\]

where \(\frac{\text{d}i}{\text{d}t}_{t > 500 \text{s}}\) is the slope of the linear portion of the current decay and \(t_0\) is the current at the start of polarization back-extrapolated from the linear current decay. It is evident from Figure 9b that the long-term poisoning effect for ethanol oxidation can be controlled on Pt30Pd38Au32/C as compared to the Pt/C electrode. This is in agreement with the results of the cyclic voltammetric experiments (Figure 7a,b). It is established that the ethanol oxidation reaction proceeds through the formation of reactive intermediates (CH3COads) and the ultimate poisoning species (COads) on the Pt group of metals. However, in the present case, it appears that the reaction in its course does not follow the same pathway for the Pt catalyst and the ternary alloy.
relationships between log \(i\) and \(1/T\) are maintained throughout the temperature range for each of the potentials. The apparent activation energy (Figure 10b) for ethanol oxidation on Pt/C increases from 9.04 to 13.55 kJ mol\(^{-1}\), whereas on Pt\(_{30}\)Pd\(_{38}\)Au\(_{32}\)/C, the same decreases from 5.44 to 4.09 kJ mol\(^{-1}\) during the shift to potential from \(-0.4\) to \(0.2\) V. Therefore, it can be suggested that alloying Pd and Au with Pt helps to lower the activation energy for ethanol oxidation. The lower values of \(E_{a(app)}\) for ethanol oxidation on Pt\(_{30}\)Pd\(_{38}\)Au\(_{32}\)/C catalysts leads to an increase in the ethanol oxidation rate on that catalyst. It is understandable that conversion of ethanol to CO\(_2\) always requires transfer of additional oxygen species from other activation species, such as H\(_2\)O and OH\(^-\), so as to overcome the limitations of sluggish kinetics as associated with the Pt catalyst. The cometals Pd and Au, in almost equal proportions, hold a strong partnership with the base metal Pt, providing their best individual capabilities of activating the surface with the formation of (OH)\(_{ads}\), as in the case of Pd, through image dipolar interactions\(^32\) and a ready supply of oxygen to the ultimate carbonaceous species by Au through surface oxide formation.

The reaction on Pt presumably keeps on proceeding toward ultimate poisoning by Pt\(_{C-CO}\) formation, thus exhibiting an unfavorable kinetics for the complete oxidation of ethanol. However, the reaction of CO\(_{ads}\) with \(OH_{ads}/OH^-\) can occur at high activation energy only when PtOH is formed at higher potentials, producing carbonates and thus alleviating the problem of surface poisoning to some extent at elevated \(T\).
temperatures. On the other hand, kinetic control is established on Pt\textsubscript{30}Pd\textsubscript{38}Au\textsubscript{32}/C by the reaction of the carbonaceous intermediates (CH\textsubscript{3}CO\textsuperscript{ads}) with OH\textsubscript{ads}, leading to the formation of CH\textsubscript{3}CO\textsuperscript{-} ions as well as formation of carbonates by facile C–C bond cleavage at a lower overpotential. These two anionic species exit the pre-electrode layers and diffused to the bulk with sufficient ease, thus rendering the surface free from blockage. Eventually, an appreciable reduction in the activation energy sufficed the pre-electrode layers and diode cleavage at a lower overpotential. These two anionic species result was obtained for methanol oxidation,\textsuperscript{33} where the induciveness is observed at all temperatures, which indicates the presence of a resistive component in the integrated circuit. The diameter of this semicircle decreased as the temperature increased. Pseudoinductive behavior (positive \( Z'' \) values) at low frequencies is observed when the temperature is raised above 20 °C. A similar result was obtained for methanol oxidation,\textsuperscript{34} where the inductive effect was attributed to the kinetics of the electrooxidation process, in particular, to CO oxidation.\textsuperscript{34–37} Bode plots are shown in the insets of Figure 11a,b. These plots show that the phase angle (\( \Phi \)) is almost independent of the temperature in the frequency range of 30 kHz to 300 kHz. At low frequency ranges, the phase angle shows a maximum; its value depends on the temperature as well as the frequency. The maximum value of the phase angle is obtained at the highest temperature studied. As the temperature is increased, the maximum in the phase angle decreased and shifted to higher frequencies. In the case of responses, obtained for temperatures above 40 °C, the phase angle values cross the frequency axis and move toward positive values of the phase angle with a displacement toward higher frequencies where the phase angle nears zero. The increasing frequency values as a function of the temperature indicates the predominance of the pseudoinductive behavior, which translates to an increase in the reaction rate with increasing temperature. This indicates that the reaction activity increased with increasing temperature, which is in concordance with the results of voltammetry. The electrooxidation of ethanol on both the catalysts shows inductive behavior only at higher temperature, which is indicative of the possible oxidation of the accumulated reaction intermediates on the catalyst surface at elevated temperatures. Therefore, with increasing temperature, the reaction kinetics is enhanced and governed by partial oxidation of ethanol, which, in effect, forms more CO\textsubscript{ads}. The impedance data were analyzed using the software available with the potentiostat (Autolab 12, FRA, version 4.9), resulting in the equivalent circuits shown in the insets of Figure 11a,b. In this circuit R\textsubscript{ct}, CPE, and R\textsubscript{ct} are representative of the solution resistance, constant phase element, and charge-transfer resistance associated with the ethanol oxidations primarily involving the dissociative adsorption of the alcohol on the surface. In another circuit, R\textsubscript{ct}, CPE, and R\textsubscript{ct} represent the solution resistance, a constant phase element corresponding to the double layer capacitance, and the charge-transfer resistance associated with the electrooxidation of ethanol. For the ternary catalyst, the circuit included the inductive resistance (R\textsubscript{i}) and the inductance (L) associated with the CO\textsubscript{ads} oxidation kinetics. The equivalent circuit parameters are summarized in Table 2. It is evident from Table 2 that very feeble charge-transfer resistance is offered by Pt\textsubscript{30}Pd\textsubscript{38}Au\textsubscript{32}/C, which is almost 30 times less than those offered by Pt alone at this temperature range (compared at 60 °C). There is a significant fall in the R\textsubscript{ct} values for this catalyst, even at a temperature as low as 20 °C, and is clearly shown in Table 2. The appearance of L and its subsequent lowering at high temperature (80 °C) for the ternary system reflects the successful oxidative removal of carbonaceous intermediates from the surface. Thus, it appears that the cometals provide tremendous kinetic input in the
reaction sequences for ethanol oxidation on the Pt–Pd–Au surface as the dehydrogenation process gets immediately coupled with faster oxygen transfer on the preactivated surface and the oxidation tends to proceed toward completion. This outstanding catalytic performance of the Pt30Pd38Au32/C system toward the charge-transfer kinetics of ethanol oxidation establishes the superiority of this electrode over Pt in an alkaline medium.

3.3. Estimation of Oxidation Products Formed during Ethanol Electrooxidation and Its Mechanistic Overview. Figure 12a,b shows the ion chromatograms for the product analysis of the constant potential (−300 mV vs Hg–HgO) oxidation of ethanol carried out on Pt/C and Pt30Pd38Au32/C electrodes for a period of 1 h at temperatures in the range of 20°–80 °C. The respective products formed, acetate and carbonate, during the oxidation of ethanol were estimated and verified under the influence of temperature. The estimated quantities of acetate and carbonate are extremely high on the Pt30Pd38Au32/C as compared to Pt/C which, however, showed a greater temperature dependence for ethanol oxidation as the temperature was raised from 20° to 80 °C.

The overall oxidation reaction equation for ethanol in an alkaline medium is supposed to be

$$\text{CH}_3\text{CH}_2\text{OH} + 12\text{OH}^- \rightarrow 2\text{CO}_2 + 9\text{H}_2\text{O} + 12\text{e}^- \quad (3)$$

However, the electrooxidation reaction of ethanol is considered to be a complex reaction that proceeds through multiple steps. Several reaction products and intermediates are expected to be formed on the catalyst surface. Some of the adsorbed intermediates converted into the end products, such as acetate and carbonate, and the rest being retained on the catalyst surface may cause considerable reduction in the fuel efficiency. Table 3 shows the yield of acetate and carbonate ions produced at each temperature for Pt30Pd38Au32/C and Pt/C catalysts. The respective yield of these two anionic products at both the catalysts showed a greater temperature dependence for ethanol oxidation as the medium. The Pt30Pd38Au32/C catalyst showed remarkable improvement in catalytic activity toward ethanol oxidation compared with Pt/C catalyst at 20 and 80 °C. The findings from the product analysis also corroborate with the results obtained from the electrochemical measurements.

A schematic of mechanistic pathways for the ethanol oxidation process on the Pt30Pd38Au32/C catalyst in alkaline media has
been proposed (Scheme 1) with the presumption that Pd and Au incorporation into the Pt matrix makes a combined effort to facilitate the adsorption of OH− and also supply the oxygen species at the electrode surface.

4. CONCLUSION

For ethanol oxidation, the onset potentials on the Pt30Pd38Au32/C catalyst show a considerable negative shift with temperature, and the values are much lower than that obtained with the Pt/C catalyst. The decay in oxidation current density is minimal for the Pt30Pd38Au32/C catalyst at all temperatures, whereas the Pt/C catalyst shows rapid current decay, indicating a higher rate of catalyst poisoning. Proportionate addition of Pd and Au into the Pt matrix drastically reduces the activation energies and the charge-transfer resistance and thereby promotes the electrocatalytic activity toward ethanol oxidation. The outstanding behavior toward electrocatalysis of the optimal ternary system is further reflected by the very high yield of acetate and carbonate during the course of ethanol oxidation in an alkaline medium.

ASSOCIATED CONTENT

Supporting Information. Additional data of electrochemistry. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*Tel: 033 2668 4561 / Fax: 033 2668 2916. E-mail: jayati_datta@rediffmail.com.

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