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Copper-Palladium core-shell bifunctional nanoelectrocatalyst for ethanol oxidation and hydrogen evolution reactions[†]

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Ethanol oxidation reaction (EOR) and hydrogen evolution reaction (HER) are two of the most important technical challenges during the manifestation of ethanol and H₂-O₂ fuel cells. Herein we explore the electrocatalytic activity of Cu@Pd core-shell nanostructures on pencil graphite (PGE) for EOR and HER. A maximum peak current density of 261±11 mA/cm² with excellent retention for 1000 potential cycling was observed for EOR. High performance liquid chromatography and Raman analysis indicates upto 12-electron transfer oxidation with the formation of carbon dioxide or carbonate, indicating the superiority of catalyst. High HER current near to its thermodynamic potential of ~ 0 V vs. RHE, together with a stable performance for 1000 voltammetric cycles, make Cu@Pd/PGE as a potential catalyst for HER in acidic media. The catalytic efficiency is also manifested by the well resolved voltammetric features during HER activity with a Tafel slope comparable to commercial Pt/C catalysts. The excellent bifunctional activity of Cu@Pd/PGE provides a new route for commercialisation of low-cost electrocatalysts for fuel cell applications.

1 Introduction

Energy is considered as globally accepted currency with an exponential increase in demand year by year. As a result, meeting the energy demand has become one of the most challenging tasks in 21st century^{1,2}. Among a variety of alternative energy resources, fuel cells are being explored as an amicable replacement for cleaner energy³. Fuel cells with their promising energy conversion rate, storage and power density are becoming highly attractive in recent years. However, high initial investment and low efficiency limit their wide-spread commercial usages. Fuel cells based on ethanol or hydrogen are expected to be the future energy resources to alleviate these limitations⁴. Challenges for the realisation of H₂-O₂ fuel cells are the availability, storage, transportation and handling of pure H₂ as fuel. These challenges together with low efficiency of the overall system increase the cost of energy derived from H₂-O₂ fuel cells.

Owing to the limitations of H₂-O₂ fuel cells, oxidation of low molecular weight alcohols have been the most popular alternative, particularly ethanol fuel cells. Direct ethanol fuel cells (DEFCs) offer excellent specific energy density (as high as 8.0

kWh/kg)⁵. They are also preferred over single carbon fuels like methanol (DMFC) and formic acid in terms of availability of fuel, environmental toxicity, ease of handling, lesser chance of fuel crossover through the membrane as well as catalyst poisoning. Ethanol can be easily obtained from sugar, starch or other biomass through fermentation method⁶. The complete oxidation of ethanol to water and carbon dioxide take place through the cleavage of C-C bond which involves exchange of 12 electrons during the entire process (represented as C₁ pathway). Alternative pathways include a 4-electron transfer reaction with formation of acetaldehyde or acetic acid as a major product (represented as C₂ pathway). However, the later loses about 67% energy of the fuel cell. Hence, the main challenge in DEFC is obtaining an efficient catalyst that can cleave C-C bond at lower potentials leading to the complete conversion.

Platinum is the most commonly used catalyst for both HER and EOR. Albeit, high cost of Pt restricts its commercial applications. Non-platinum electrocatalysts including but not limited to transition metals (Pd, Ni, Mo, W, Ru), transition-metal-based alloys (eg. Cu-Pd or Au-Pd) as well as graphene based metal/metal oxide composites open up wide scope for the development of efficient electrocatalysts⁷⁻⁹. Recent studies have demonstrated excellent electrocatalytic efficiency of Pd towards HER and EOR. Compared to Pt electrocatalysts, Pd provides additional advantage of less catalyst poisoning with carbon monoxide during EOR. Various core-shell nanoparticles and nanostructures have shown

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promising results since their particle size, morphology and composition can be easily adjusted in a defined way to tune their physicochemical properties. Compared to monometallic nanostructures, core-shell nanostructures (eg. Au@Pt, Au@Pd, Pt@Pd, Pd@Pt) exhibited superior catalytic efficiency which is not attainable by their monometallic counterparts^{10–13}. For example, Au@Pt and Pd@Pt core-shell nanostructures exhibited enhanced CO tolerance during EOR compared to bare Pt nanostructures¹⁴.

Palladium is also well known for its hydrogen adsorption capabilities. Nanosized palladium or a thin layer of deposited palladium are shown to provide better adsorption and hydrogen evolution reactions¹⁵. Core-shell nanostructures with Pd shell and a non-precious metal such as copper were used to reduce the Pd loading without compromising the catalytic activity¹⁶. In the strategy presented here, we make use of the synergistic effect of Cu with Pd, which also facilitates lower amount of Pd loading on a cost-effective pencil graphite substrate. We show the promising bifunctional electrocatalytic properties of copper-palladium dendritic core-shell nanostructures towards hydrogen evolution and ethanol oxidation reactions that are much superior to many of the recently reported electrocatalysts.

2 Materials and Methods

2.1 Materials

Pencil graphite lead (PGE, Faber Castell Polymer Lead HB) of 0.7 mm diameter was used as the substrate for catalyst modification. Perchloric acid (HClO₄) was procured from Merck-Millipore while sodium dodecyl sulfate (SDS), potassium chloride (KCl), sodium sulfate (Na₂SO₄), copper sulfate (CuSO₄), palladium chloride (PdCl₂), sulfuric acid (H₂SO₄), potassium bicarbonate (KHCO₃), potassium carbonate (K₂CO₃), acetaldehyde (CH₃CHO), acetic acid (CH₃COOH), potassium acetate (CH₃COOK), potassium hydroxide (KOH) and ethanol were purchased from Sigma-Aldrich and were used as received. Commercially available 20 % platinum on carbon (Pt/C) was used for comparison during HER reaction. Deionized water was used to prepare all the aqueous electrolytes.

All the experiments were performed in a conventional three electrode cell connected to an electrochemical workstation (CHI660E, CH Instruments, USA). Electrodeposition of copper on pencil graphite (Cu/PGE) was carried out by following our earlier report¹⁷. Briefly, the deposition was carried out at -0.7 V vs. SCE in a solution containing 15 mM CuSO₄ as copper precursor and 0.1 M Na₂SO₄ as supporting electrolyte in presence of SDS as a soft template for a duration of 300 s. Galvanic replacement reaction (GRR) of Pd on Cu/PGE for the preparation of Cu@Pd core-shell nanostructures was carried out by using 1 mM PdCl₂ solution¹⁸. It was observed that direct deposition of Pd on PGE was not stable to carry out any electrocatalytic studies due to low adhesion of Pd directly onto the PGE. Hence copper provided a good adhesive surface for Pd deposition. Cyclic voltammetric and amperometric studies were performed using Cu@Pd/PGE as working electrode, platinum wire as counter electrode and Ag/AgCl (satd. KCl) or saturated calomel electrode as reference electrode. For the HER, these potentials were converted to the RHE scale. Elec-

trochemical impedance analysis were performed in a frequency range of 1 Hz to 100 kHz. Both EOR and HER studies were carried out in a 15 mL electrochemical cell.

The morphology of the prepared Cu@Pd/PGE nanostructures were obtained through scanning electron microscopy (SEM, Vega 3 TESCAN, VEGA 3 SDH 116-0136) and/or field emission scanning electron microscopy (FESEM) with energy dispersive X-ray analysis (EDAX) (JEOLJSM-6701F) and transmission electron microscope (TEM, PHILIP, CM 200 model). High performance liquid chromatography (HPLC) analysis was performed with Hi plex H Agilent reverse phase column (300*7.7 mm) as stationary phase and 0.005 M sulfuric acid as eluent (mobile phase). The column was maintained at room temperature throughout the analysis. Flow rate of 1 mL per minute and injection volume of 200 µL were maintained in all the experiments using different concentrations of the standards. Raman spectra were obtained using B&W TeK iRaman plus spectrometer with 532 nm cw laser light as an excitation source. Measurements were carried out with 15 mW of laser power.

3 Results and Discussion

3.1 Physical characterisation

Representative SEM images of the copper-palladium modified pencil graphite substrate (Cu@Pd/PGE) is presented in Fig. 1(A-B). In comparison with the electrodeposited copper on pencil graphite, Cu@Pd/PGE exhibits dendritic nanostructures, and resembles the morphologies of copper adatoms that were prepared by the template electrodeposition method^{17,18}. The vertical growth of dendritic structures also provided a good porosity for the material as evidenced from these figures. From the EDAX data through Fig. 1(C), elemental ratio was obtained and the details are presented in the appended table. Atomic ratio between Cu and Pd on the sample was calculated to be 37.7:62.3. The high amount of Cu in the present studies compared to our earlier reports (17.44 : 82.56)¹⁸ may be due to the variation in the copper deposition. Previously Cu deposition was carried out for 120 s while in the present studies, the deposition was carried out for 300 s, which is expected to increase the copper loading on the PGE surface. A small amount of carbon and chlorine observed through EDAX analysis may be attributed to the exposed PG surface and adsorbed chloride ions due to PdCl₂.

XPS full spectrum shown in Fig. 1(D) displays response peaks for carbon, palladium, oxygen and copper. The spectrum of palladium in Fig. 1(E) shows a doublet peak, which can be attributed to Pd_{3/2} and Pd_{5/2} with core-level binding energy (B.E.) of 340.78 eV and 336.95 eV respectively, that are in good agreement with the literature reports^{19–22}. Core-shell palladium showed a shift in the binding energy levels towards positive side compared to palladium nanoparticle, where Pd_{3/2} and Pd_{5/2} binding energies were found to be 340.4 eV and 335.1 eV, respectively²³. The positive shift in the binding energy of these bimetallic palladium is due to the presence of copper, which results in loss of electron from surface palladium²⁴. A small satellite peak at 337.48 eV may be ascribed to the trace amount of Pd in its oxide form as Pd(II) that are formed during the galvanic replacement reaction²⁵. The

Fig. 1 Scanning electron microscopic image of Cu@Pd/PGE at different magnifications (A-B), EDAX analysis of Cu@Pd/PGE (C), XPS spectra of Cu@Pd/PGE electrode: Full spectra (D) and Pd spectrum (E) and the elemental mapping of the nanostructures showing the distribution of Cu and Pd (F)

small peak at 950 eV could be attributed to the $\text{Cu}2\text{P}_{1/2}$ ^{21,26,27}. Fig. 1(F) represents the distribution of Cu and Pd respectively on the PG surface, indicating a homogenous distribution.

TEM images provided through Fig. 2(A) also indicates small spherical core-shell particles with dendritic structures on the surface of pencil graphite substrate. A closer look at the images shown in Fig. 2 (B) and (C) indicate that a thin layer of palladium is formed on the surface of copper. The palladium deposition on copper surface is observed to be of a few atomic layer thick and continuous without any interruption. Fig. 2 (D) presents the embedded Cu@Pd nanostructures which were formed as spherical nanostructures apart from dendritic structures. These images are in good agreement with our earlier studies, where formation of spherical nanostructures with size of below 10 nm were demonstrated with galvanic replacement reactions¹⁸. High resolution image provided in Fig. 2(D-F) indicate SAED pattern with lattice fringes of these Cu@Pd/PGE nanostructures. Lattice distance was calculated to be 0.223 nm which corresponds to (111) plane of FCC structure of Cu@Pd nanostructures, that are supported on pencil graphite substrate. XRD data of the samples indicated the presence of (111), (200), (311) planes of Pd on the copper surface¹⁸.

To further understand the structural aspects of the prepared material, cyclic voltammetry (CV) was carried out in 0.1 M phosphate buffer solution (PBS, 7.4 pH). As shown in Fig. S1(A) (Supporting Information), the CV of copper modified PGE (Cu/PGE) exhibited the oxidation peak at around +0.2 V and a reduction peak at around -0.2 V (both vs. Ag/AgCl). However, after the palladium modification as represented in Fig. S1(B) (Supporting Information), these peaks were completely disappeared. The

new peaks at around 0.0 V could be assigned to the oxide growth on the surface of palladium to form Pd(II) or higher oxidation states²⁸. The anodic peak with an onset potential of about 1 V could be attributed to the oxygen evolution reaction. The oxide stripping peak is observed around 0 V as a cathodic peak. On the other hand, CV in ferrocyanide/ferricyanide solution provided only one oxidation and reduction peak at around +0.3 V and +0.2 V respectively as shown in Fig. S1(C) (Supporting Information). These peaks are characteristics of the redox reaction of ferrocyanide/ferricyanide. Moreover, presence of copper on the surface should have lead to the formation of prussian blue (copper ferrocyanide). These observations prove that copper on the electrode surface is not exposed to the electrolyte. A plot of current density vs. square root of scan rate (J vs. $\nu^{1/2}$) is provided in Fig. S1(D) (Supporting Information). A linear variation of anodic and cathodic peak current density against $\nu^{1/2}$ show that the ferrocyanide/ferricyanide reaction is under diffusion controlled regime. Combining the information received from the physical and electrochemical analysis, it may be concluded that the prepared copper-palladium nanostructures are core-shell in nature where copper is surrounded by palladium atoms.

To evaluate the catalytic efficiency of the prepared Cu@Pd/PGE core-shell nanostructures, ethanol oxidation reaction (EOR) was carried out in alkaline media while hydrogen evolution reaction (HER) was analysed in acidic media.

3.2 Ethanol oxidation reaction (EOR)

The performance of Cu@Pd/PGE electrodes was initially tested in both acidic (1 M HClO_4) and basic media (1 M KOH) using cyclic voltammetry. In acidic media as shown in Fig. 3(A), the

Fig. 2 Transmission electron microscopic image of palladium modified Cu/PGE at various magnifications (A-C); SAED pattern (D) and lattice distance measurements (E-F)

anodic peak with an onset potential of around 0.7 V was observed and a corresponding cathodic peak at around 0.55 V (vs. Ag/AgCl). However, these peaks were present even in the absence of ethanol, and the peak behavior did not change much with different concentrations of ethanol. This indicates that these two peaks could be attributed to the surface oxidation and oxide stripping of palladium.

In alkaline media, as presented in Fig. 3(B) two well defined peaks were observed, one during forward scan (f-peak) with an onset potential of -0.7 V and one during the reverse scan (b-peak) at -0.35 V. These peaks are in accordance with the butterfly region reported in the literature for ethanol oxidation reaction on various electrocatalysts^{29–33}. The f-peak is typically attributed to the oxidation of ethanol adsorbed over the catalyst surface and the b-peak is assigned to the oxidation of adsorbed carbonaceous species of ethanol dissociation. A maximum current density for the anodic peak was estimated to be 261 ± 11 mA/cm² at -0.027 V. The adsorption of hydroxyl groups in alkaline media, not only influence the reaction steps but also enhances the rate of EOR^{34,35}.

Specific adsorption of various intermediate anions are known to affect the electrochemical catalysis. The mechanism behind the changes in catalytic activity could be attributed to the blocking of active sites of the catalyst, and thereby altering adsorption energy states of the catalyst and/or surface modification³⁶. In the present studies, in acidic medium, the presence of perchlorate species is significant, which inhibits the adsorption and oxidation of ethanol on the surface. In alkaline media, adsorption of hydroxyl and/or alkoxy groups derived from ethanol are more prominent³⁷. Moreover, in basic solution, ethanol is deprotonated and acts as a stronger ligand, while in acidic solution, ethanol

deprotonation is absent. To summarise the comparison, alkaline media was chosen for further studies due to observed catalytic activity that was resulted from the adsorption of oxygen species. Moreover, the major charge carriers are OH⁻ ions in the alkaline media, which may reduce the fuel crossover compared to acidic media during the running of fuel cells. Further, the optimum concentration of KOH for maximum catalytic performance was found to be 1 M, as concluded from Fig. S2 (Supporting Information).

In order to study the morphological variation on the catalytic activity, copper nanostructures were prepared with different deposition conditions. Our previous studies have shown that the potential of electrodeposition influence the morphology of deposited copper nanostructures¹⁷. Further, it was observed that Pd deposition follows the nanoarchitecture of the copper adatoms. To study the consequences of these changes on the electrocatalytic properties, copper deposition was carried out at three different potentials viz. -0.5 V, -0.7 V and -0.9 V (all potentials vs SCE), followed by galvanic replacement reaction for Pd deposition. These three samples are represented as Cu@Pd/PGE(-0.5), Cu@Pd/PGE(-0.7) and Cu@Pd/PGE(-0.9) respectively. EOR catalytic activities of these electrodes were studied in an aqueous solution containing 1 M KOH and 1 M ethanol and the results are provided in Fig. S3 (Supporting Information). From the CV, ratio of current densities corresponding to forward and backward peaks (J_f/J_b) were calculated. Previous reports have suggested the comparison of J_f/J_b ratio before and after potential cycling as a tool for evaluating the catalyst poisoning and tolerance towards intermediate carbonaceous species, which are valuable information regarding catalyst performance^{38,39}. Although voltammetric profiles are similar in shape for all the three electrodes, significant

Fig. 3 Cyclic voltammogram of Cu@Pd/PGE in 1 M ethanol solution using 1 M HClO₄ (A) and 1 M KOH (B) as electrolyte. Long term stability towards EOR in 1 M KOH and 1 M ethanol (C), comparison of electrochemical active surface area before and after 1000 potential cycles towards EOR (D), Tafel slope analysis of Cu@Pd/PGE towards EOR (E) and Electrochemical impedance analysis of Cu@Pd/PGE at various potentials in 1 M ethanol and 1 M KOH (F)

differences were observed in their current values.

The onset potential was observed to be around -0.7 V for all three electrodes, which facilitates adsorption of alcoholic groups. The three electrodes were subjected to 300 potential cycles (CV) in the electrolyte. As represented in the Table S1 (Supporting Information), the Cu@Pd/PGE(-0.9) showed a significant decrease in J_f/J_b ratio from 3.24 to 2.47 indicating a diminished activity whereas for Cu@Pd/PGE(-0.5) and Cu@Pd/PGE(-0.7), the current ratio was not much deteriorated with potential cycling. The J_f and J_b values for Cu@Pd/PGE(-0.5) for the first cycle were 154.2 mA/cm² and 51.88 mA/cm² respectively which were much less than that for Cu@Pd/PGE(-0.7) (223.14 mA/cm² and 84.2 mA/cm² respectively). This indicates the superior catalytic performance with excellent retention of activity by Cu@Pd/PGE(-0.7) towards EOR and hence all further studies were carried out using the same catalyst.

The catalyst deactivation and thereby stability parameters were evaluated using cyclic voltammetry and the corresponding peak current density vs cycle number (in 1 M KOH and 1 M ethanol) are presented in Fig. 3(C). The catalytic activity decayed from its initial value of 261 ± 11 mA/cm² to 186.5 ± 5.63 mA/cm² and then decreased gradually to 169.84 ± 3.43 mA/cm² at 200 cycles and finally reached a value of 47.6 ± 5.3 mA/cm² after 1000 cycles. The decrease in the catalytic activity can be attributed to the partial degradation of catalyst and/or passivation of electrode surface by intermediate species^{38–41}. To obtain more insights into the activity of catalyst before and after potential cycling in ethanol solution, electrochemical active surface area (ECSA) was evaluated in 0.3 M KOH solution by comparing the charge under oxide stripping with standard values¹⁸. From the data presented in Fig. 3(D), a decay in ECSA by 48.8 % after 1000 cycles was observed. This is in accordance with the morphology of the catalyst evaluated after 1000 potential cycling. As shown in the SEM images in

Fig. S4 (Supporting Information), the surface has been partially modified compared to the freshly prepared catalyst. Nonetheless, dendritic structures are retained to a large extent. Hence the reduction in ECSA as well as the ethanol oxidation activity could be related to the partial degradation of the catalyst surface. Changes in the electrochemical behavior after potential cycling (especially in the hydrogen underpotential deposition region around -0.8 V) may be assigned due to the change in porosity of the material, as evidenced from the SEM images. However, the catalytic retention in our studies are much superior compared to other previously reported values in the literature^{42–47}. A detailed comparison on the catalytic performance is provided at a later part. The higher initial current density and its retention after 1000 cycles indicate excellent catalytic activity and better stability with less catalyst poisoning of Cu@Pd/PGE.

Fig. 4 Raman spectra of solution containing electrolyte (1 M ethanol and 1 M KOH) (a); the electrolyte after 1000 potential cycles (b); surface enhanced Raman spectroscopy (SERS) of Cu@Pd/PGE in pure acetaldehyde (c) and SERS of the Cu@Pd/PGE after 1000 potential cycles in 1 M ethanol and 1 M KOH (d)

For obtaining quantitative information on the kinetic parameters of the catalysis, Tafel plot analysis was carried out where the overpotential (η) is plotted against $\log(J)$, where J is the current density. The results are presented in Fig. 3(E). Three linear re-

Table 1 Raman modes observed in the solution after catalysis

Peak position (cm ⁻¹)	Tentative assignment
840	ν_s (C-C)
1030	ν_s (C-O)
1080	ρ (C-H)
1326	δ (C-H) in acetic acid
1369	δ (C-H) in acetaldehyde
1446	ν_s (COO ⁻)
1579	ν_{as} (COO ⁻)
1620	δ (HOH)
2105	-CO Bridge bonding
2600	ν_s (O-H)

gions of Tafel slopes were obtained (named as a, b and c) and the slopes of each region were calculated to be 79.9, 20.5 and 10 mV dec⁻¹ in the potential ranges of -0.72 to -0.60 V, -0.60 to -0.50 V and -0.50 V to -0.47 V respectively. The high Tafel slope values at higher negative potentials (region-a) corresponds to adsorption of hydroxyl groups over the electrode surface. As the potential is shifted to lower negative values (region b & region c), the slope is very minimal and the decrease in the slope value indicates the facile kinetics of the ethanol oxidation on the catalyst surface^{29,48}.

In-depth knowledge on catalytic efficiency was further obtained by electrochemical impedance analysis (EIS) carried out at various potentials (-0.9 to -0.2 V) and the corresponding Nyquist plots are provided in Fig. 3(F). As noted, the semicircle at high frequency region corresponding to the charge transfer resistance (R_{ct}) of the ethanol oxidation process initially increases upto -0.7 V and then decreases. The initial increase may be due to the reduced water splitting reaction. Further reduction in R_{ct} values at higher positive potentials could be correlated to the facile ethanol oxidation reaction. These results are in agreement with our cyclic voltammetric data obtained through Fig. 3(A), where the onset potential for EOR was found to be -0.7 V.

Since complete oxidation of ethanol involves a 12-electron transfer reaction, the products formed during electrocatalysis could be correlated to be catalytic efficiency. Typical products of ethanol oxidation are acetaldehyde (CH₃CHO), acetic acid (CH₃COOH), carbon monoxide (CO) and carbon dioxide (CO₂, which may present as K₂CO₃ in alkaline media). The mechanistic challenge of EOR lies in determining the pathway which gives carbon dioxide as the major product. Raman spectroscopy and high performance liquid chromatography (HPLC) were utilized for identification of intermediates and the final products. Fig. S5-S7 (Supporting Information) represent the HPLC data of the standards of various reaction intermediates in EOR. The retention times (RT) for CH₃COOH, CH₃CHO, K₂CO₃, CH₃COOK and ethanol were obtained as 16.27, 18.44, 19.82, 16.25 and 21.35 min respectively. However, RT for CH₃COOK and CH₃COOH were overlapping at 16.25 min. K₂CO₃ showed a negative peak in the HPLC analysis, hence the standards were taken in negative polarity for quantification. Calibration graph was obtained for different concentrations of standards (0.01 M, 0.03 M, 0.05 M, 0.07 M and 0.1 M) by plotting the concentration vs peak area. For identifying the reaction products during our catalytic process, samples

were collected after ethanol oxidation reaction for 1000 cycles, which were subsequently analysed by HPLC and the results are presented in Fig. S8 (Supporting Information). From the sample analysis, two sharp peaks at RT 16.25 min and 21.8 min were observed corresponding to CH₃COOK or CH₃COOH and ethanol respectively. As the electrolyte contains high concentrations of KOH, CH₃COOK formation is expected over CH₃COOH. The small negative peak at RT 20.1 min could be assigned to K₂CO₃. Only trace amount of CH₃CHO formation was observed at a RT value of 18.2 min. as shown in Fig. S9 (Supporting Information). The concentrations of the products formed after 1000 cycles of EOR were calculated to be 0.035 M of CH₃COOK and 0.033 M of K₂CO₃.

Fig. 4(a-b) represents the Raman spectra of the electrolyte (1 M ethanol + 1 M KOH) before and after 1000 catalytic cycles using Cu@Pd/PGE. The tentative peak assignments are provided in Table 1. In accordance with the literature reports, spectra recorded in aqueous electrolytes were dominated by the presence of strong peaks at 1600 cm⁻¹ and 3270 cm⁻¹ which could be assigned to H-O-H bending and O-H stretching vibrations^{43,49,50}. The two sharp peaks at 1440 cm⁻¹ and 1580 cm⁻¹ could be assigned to the characteristic symmetric and asymmetric stretching modes of the O-C-O group of the acetate ions⁴³. The broad peak in the range of 1300 cm⁻¹ - 1348 cm⁻¹ are typically attributed to the overlap of bending vibrations of -CH₃ group of acetates or adsorbed acetates. These peaks are in agreement with the peaks obtained for various acetate ions, as shown in Fig. S10 (Supporting Information). Upon the total oxidation of ethanol in alkaline media, carbonates (CO₃²⁻) are the only species which are very stable and a peak at 1370 cm⁻¹ confirms the presence of carbonates in this experiment which is in good agreement with the HPLC results discussed above^{31,43,51}.

The presence of carbonates at very low potentials is an indication of total ethanol oxidation (resulting from the dissolution of CO₂ in alkaline electrolyte). Formation of CO₂ is assumed through specific adsorption of ethanol on the electrode surface which leads to C-C scission before nucleation with hydroxyl groups⁴³. Formation of CO₂ is preceded by the formation of CO_{ad}, although identification of CO in alkaline electrolyte is very difficult. However, Raman bands in the region of 1800 cm⁻¹ to 2200 cm⁻¹ were attributed to C-O stretching in alkaline media^{49,52,53}. Fig. 4(c) represents the surface enhanced Raman spectra of the Cu@Pd/PGE after 1000 potential cycling. The peak at 1960 cm⁻¹ could be assigned to C-O bridge bonding and a broad band from 2000 cm⁻¹ - 2030 cm⁻¹ could be ascribed to the C-O linear bonding. Rapid oxidation of CO_{ad} to CO₂ may not give clear peaks at the prescribed regions. These results are in agreement with the Raman spectra obtained for the pure samples of the intermediates as presented in Fig. S10 (Supporting Information).

It has been reported that two major parameters which are significant in deciding the C₁ or C₂ pathways are the nature of catalyst and electrolyte. Both these parameters can significantly influence the adsorption of ethanol or other intermediates on the electrode surface^{19,49,50,54,55}. If the adsorption of hydroxyl species predominates, the oxidation may preferably take place through C₂ pathway and acetic acid as the main product. On the other

Scheme 1 Plausible schematic representation of ethanol oxidation reaction on Cu@Pd/PGE surface in 1 M KOH solution

hand the adsorption of acetaldehyde over the catalyst surface dominates in the C_1 pathway where C-C scission takes place and forms CO_2 (or carbonate in alkaline media) as the final product. The presence of both acetate and carbonate species observed in our studies indicates possible reaction pathway through acetaldehyde adsorption which further undergoes oxidation to either CO_2 or acetate. A schematic representation of the plausible reaction pathway is demonstrated in Scheme 1.

This is also supported by the fact that ethanol adsorption is more prominent on a palladium surface due to the better ligand strength of ethanolate ion. Hence the reaction is expected to be going through Eley-Rideal mechanism, where adsorbed ethanolate ions react with hydroxyl ions in the solution and leading to the formation of various adsorbed species and the final products as depicted in the scheme. The proposed mechanism is also in accordance with recently reported mechanism for ethanol oxidation reactions^{56,57}. HPLC analysis indicated a trace amount of acetaldehyde that was formed during catalysis, which was not sufficient enough to quantify as shown in Fig. S9 (Supporting Information). Surface enhanced Raman analysis (SERS) of Cu@Pd/PGE immediately after the electrochemical catalytic cycling further supports the acetaldehyde adsorption on the Pd surface, as shown in Fig. 4(c-d). Moreover, the C-C bond breaking is expected through the specific adsorption of oxygen containing intermediates over the catalyst surface. The strong adsorption enhances the kinetics of EOR and reduces the catalyst poisoning as all the surface intermediate species formed are not strongly adsorbed in alkaline media⁴⁹.

The superiority of the Cu@Pd/PGE towards EOR is also emphasised by the excellent catalytic retention which is much superior compared to many literature reports using similar catalytic materials. A detailed comparison in terms of catalytic performance containing Pt and/or Pd based electrocatalysts are presented in Table S2 and Table S3 (Supporting Information). Some of them provided higher retention of activity after 1000 cycles, however, they had relatively lower initial catalytic current. Higher current density at the beginning and end of potential cycling along with less catalytic poisoning and good retention of catalytic activity indicate the promising application of Cu@Pd/PGE with good stability towards ethanol oxidation.

3.3 Hydrogen Evolution Reaction(HER)

For the study of hydrogen evolution reaction (HER), the availability of protons are of significant importance. As a result, the reaction is most feasible in acidic conditions. In the present studies, we have used H_2SO_4 as the electrolyte medium. Linear sweep voltammetry (LSV) was used for preliminary understanding using Cu/PGE, Cu@Pd/PGE as well as commercial Pt/C catalysts and the results are presented in Fig. 5(A-B) where the current densities are corrected for geometrical surface area and electrochemical surface area respectively. While Cu/PGE showed HER with an onset potential of -1.3 V vs RHE, Cu@Pd/PGE exhibited HER with an onset potential of -0.07 V vs RHE. Maximum current density of 18 mA/cm^2 was observed for Cu/PGE at an overpotential (η) of -1.4 V vs RHE whereas Cu@Pd/PGE exhibited current density of 157 mA/cm^2 at an overpotential of -150 mV vs RHE. In comparison with these two catalysts, commercially available platinum supported on carbon (Pt/C) under similar conditions showed an onset potential of 0.03 V vs RHE and current density of 80 mA/cm^2 . This indicates that catalytic efficiency of Cu@Pd/PGE is much superior compared to commercial platinum samples, the enhancement may be attributed to high catalyst loading and/or high electrochemically active surface area. It may be noted that the new catalyst presented here provides an excellent current density that is comparable to the commercial Pt/C even after corrected for the electrochemical surface area, as evidenced from Fig. 5(B).

To optimise the concentration of electrolyte, HER current response was monitored using cyclic voltammetry in different concentrations of H_2SO_4 ranging from 0.1 M to 0.5 M and the results are provided in Fig. 5(C). A maximum current density of 157 mA/cm^2 was observed for 0.5 M H_2SO_4 and hence all further experiments were carried out at the same concentration. Further insight into the catalytic activity was obtained by analysing the cyclic voltammogram in detail. Typically, during the HER, two asymmetric anodic and cathodic peaks are observed very close to 0.05 V vs RHE which are attributed to hydrogen adsorption and desorption on palladium. Current response due to hydrogen adsorption and desorption was increased with increase in electrolyte concentration while peak separation between $H_{\text{adsorption}}$ and $H_{\text{desorption}}$ was narrowed down to 35 mV. As represented in Fig. 5(D), transient a and e refer to underpotential deposition of

Fig. 5 Linear sweep voltammetry of Cu/PGE (a), Cu@Pd/PGE (b) and commercial Pt/C (c) in 0.5 M H₂SO₄ at 0.01 V/s scan rate where current is corrected for geometrical surface area (A); Linear sweep voltammetry of Cu/PGE (a), Cu@Pd/PGE (b) and commercial Pt/C (c) in 0.5 M H₂SO₄ at 0.01 V/s scan rate where current is corrected for electrochemical surface area (B); Cyclic voltammetry of Cu@Pd/PGE in different concentrations of H₂SO₄ (a) 0.1 M (b) 0.2 M, (c) 0.3 M and (d) 0.5 M, at a scan rate of 0.01 V/s (C) and cyclic voltammetric profile of Cu@Pd/PGE featuring the hydrogen adsorption and desorption process (D)

hydrogen (H_{UPD}), transients **b** and **d** refer to adsorption of under-potentially deposited hydrogen and desorption of adsorbed (H_{ad}) hydrogen from the palladium surface. Transient **c** refers to hydrogen evolution reaction. The asymmetric anodic and cathodic peak separation for H_{UPD} adsorption and H_{UPD} desorption with 35 mV shows the purely adsorptive behavior whereas peak separation of > 100 mV was exhibited on other Pd based catalysts such as Pd-CN_x over which mixed response was observed⁵⁸. From the observations, it may be summarised that at low concentrations, the reaction may be mixed response while at higher concentrations of electrolyte, it is adsorption limited reaction^{59,60}. This is also in agreement with the Tafel slope values of 90.84 mV/dec (0.1 M), 83.24 mV/dec (0.2 M) and 67.54 mV/dec (0.3 M).

Fig. 6 Tafel analysis of Cu@Pd/PGE electrode and commercial Pt/C for the hydrogen evolution reaction (A); Electrochemical impedance analysis of Cu@Pd/PGE towards HER (B); HER current measured at -0.2 V vs RHE towards HER for 1000 cycles using Cu@Pd/PGE (C) and chronoamperometric response of Cu@Pd/PGE at -0.2 V vs RHE (D)

Table 2 Parameters of fitting for the electrochemical impedance analysis using the R(C(RW)) or R(CR) equivalent circuit

Overpotential η (mV vs RHE)	R_u (Ω)	C_{dl} (μF)	R_{ct} (Ω)	Z_w $S.s^{1/2}.cm^2.A^{-1}$
100	2.56	4.38	140.80	0.01
50	2.56	4.36	112.20	0.02
0	2.54	4.05	47.20	0.21
-50	5.01	9.08	30.27	-
-100	5.03	7.99	17.95	-
-150	5.06	7.30	11.64	-
-200	5.08	6.13	8.41	-
-250	5.01	5.77	6.72	-

For obtaining kinetic parameters of hydrogen evolution reaction on Cu@Pd/PGE surface, Tafel plot analysis was performed and the plot of the log of current density ($\log(J)$) as a function of overpotential (η) is shown in Fig. 6(A). The Tafel slope was used to evaluate the kinetic feasibility of reaction. Tafel analysis is provided for a commercial platinum electrode as well for the purpose of comparison in Fig. 6(A). Commercial Pt surface, a well-known catalytic material for hydrogen evolution reaction, had a Tafel slope of 31.65 mV dec⁻¹. On the other side, Cu@Pd/PGE exhibited a Tafel slope of 40.3 mV dec⁻¹, which is very close to the value obtained for commercial Pt/C, indicating a facile kinetics of HER on the Cu@Pd/PGE surface. A major reason for this may be due to the change in material as platinum is known to be the most effective catalyst for HER compared to any other materials⁶¹. However, the catalytic performance of Cu@Pd/PGE is much superior compared to other non-platinum materials as demonstrated in Table S4 (Supporting Information). Typically, copper and palladium-based materials are commonly used for HER reactions apart from Pt-based materials. In comparison to many of those catalysts, Cu@Pd/PGE proposed in the present work exhibits better catalytic performance in terms of Tafel slope and hydrogen overpotential values.

Electrochemical impedance spectroscopy (EIS) was carried out in a frequency range of 1 Hz to 100 kHz at different applied overpotentials (from 0.1 V to -0.25 V vs RHE) with an ac amplitude of 5 mV. The corresponding Nyquist plots are represented in Fig. 6(B). At low positive overpotentials (+0.1 V to 0 V), a diffusion controlled regime was observed in the EIS measurement, which could be attributed to the diffusion of hydrogen ions towards adsorption on the electrode surface arising from the diffusion of protons through the porous electrode. The modified Randle's circuit, R(C(RW)), was used to fit the data in this region. When the negative overpotential was applied, the EIS data exhibited a pure kinetically controlled behavior, and the EIS data were fitted with a R(CR) circuit. The details of fitted parameters are presented in Table 2. It was observed that Cu@Pd/PGE exhibited much lower impedance at higher potentials as manifested by the smallest semicircle and corresponding low R_{ct} values. The significant reduction in the impedance allows much faster HER kinetics and improves the rate of hydrogen evolution on the copper-palladium core-shell nanostructured electrode surface.

Practical applications of catalyst depends on the durability of the catalyst. The durability of the Cu@Pd/PGE as an electro-

catalyst for HER was examined by subjecting for 1000 potential cycling. Cycle life performance presented in Fig. 6(C) shows a retention of 80.4 % compared to the initial value. Fig. 6(D) indicates the time dependant stability of the catalyst for a duration of 20 h at a potential of -0.2 V vs. RHE and a retention of 85.47 % of initial activity was observed, indicating the suitability of Cu@Pd/PGE for hydrogen evolution reactions.

Data provided in Table S4(Supporting Information) shows that porous Pd-CN_x exhibits the lowest overpotential and lowest Tafel slope for hydrogen evolution reaction but Pd/C shows the highest overpotential and Tafel slope. This may be because of faster electron transfer due to the N doped Carbon substrate. From the table, it is clear that core-shell materials such as PdCu@Pd Nanocube and Co@Pd nanocrystals exhibit better catalytic performance in terms of lower Tafel slope and lower overpotentials compared to alloy materials such as Au-Pd/carbon fiber paper and 3D Cu-Pd alloy followed by pure metal supported on conducting substrates such as Pd/HOPG or Pd/C. Compared to these electrocatalysts, Cu@Pd/PGE catalyst presented in this work exhibited better performance with reference to overpotential and Tafel slope with good retention activity.

In summary, we have demonstrated the excellent catalytic activity fo the copper-palladium core-shell nanostructures on a pencil graphite substrate for both ethanol oxidation and hydrogen evolution reactions. The proposed catalyst is observed to be very efficient in terms of catalytic activity as well as the stability. Through the data presented in Fig. S11 (Supporting Information), it is concluded that the catalyst properties are not much deteriorated even after 1000 potential cycling towards EOR or HER, indicating the promising properties of Cu@Pd/PGE for the next generation fuel cell catalysts.

4 Conclusion

In summary, the electrocatalytic activity of copper-palladium core-shell nanostructures on a cost-effective pencil graphie substrate (Cu@Pd/PGE) are demonstrated for two important fuel cell reactions, viz. ethanol oxidation and hydrogen evolution reactions. In both the reactions, the catalyst exhibited excellent performance with promising cycle life stability. Hence we conclude that these bimetallic core-shell nanostructures may be highly useful in the development of efficient and commercially viable fuel cells in the future.

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