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S. D. Senanayake, M. Guinel, and C. R. Cabrera**

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Rotating Disk Slurry Au Electrodeposition at Unsupported Carbon Vulcan XC-72 and Ce³⁺ Impregnation for Ethanol Oxidation in Alkaline Media

Luis E. Betancourt¹, Rolando Guzmán-Blas¹, Si Luo², Dario J. Stacchiola², Sanjaya D. Senanayake², Maxime Guinel¹, and Carlos R. Cabrera^{1}*

¹Department of Chemistry, University of Puerto Rico, Río Piedras Campus,

San Juan PR 00936-8377

²Chemistry Department, Building 555, Brookhaven National Laboratory, Upton, NY 11973

Abstract. A robust electrodeposition method consisting of the Rotating Disk Slurry Electrode (RoDSE) technique to obtain Au nanoparticles highly dispersed on a conductive carbonaceous support, i.e. Vulcan XC-72R, for ethanol electrooxidation reaction in alkaline media was developed. Ceria was used as a co-catalyst using a Ce(III)-EDTA impregnation method in order to enhance the catalytic activity and improve the catalyst's overall stability. The RoDSE method used to obtain highly dispersed Au nanoparticles does not require the use of a reducing agent or stabilizing agent and the noble-metal loading was controlled by the addition and tuning of the metal precursor concentration. Inductively coupled plasma and thermogravimetric analysis indicated that the Au loading in the catalyst was 9%. Particle size and characteristic Au fcc crystal facets were determined by X-ray diffraction. The morphology of the catalyst was also investigated using electron microscopy techniques. In addition, X-ray absorption spectroscopy was used to corroborate the presence and identify the oxidation state of Ce in the system and to observe if there are any electronic interactions within the 8% Au/CeO_x/C system. Cyclic voltammetry of electrodeposited 9% Au/C and Ce promoted 8% Au/C showed a higher catalytic current density for ethanol oxidation when compared with commercially available catalysts (20% Au/C) of a higher precious metal loading. In addition, we report a higher stability towards the ethanol electrooxidation process, which was corroborated by 1 mV/s linear sweep voltammetry and chronoamperometric studies.

Keywords. Au nanoparticles, Ceria, nanomaterials, ethanol oxidation, RoDSE

Introduction

Fuel Cell technology has emerged as a fully employable technological tool that could help decrease our current fossil fuel dependence while also lowering harmful gas emissions. For this purpose, platinum has been the benchmark catalyst for catalytic oxidation of hydrogen and simple alcohols due to its high activity at relatively low overpotentials, however it is severely poisoned by CO and by the chemisorption of intermediate species on Pt active sites during oxidation[1-4]. Gold is considered to be among the most inert of all metals, however studies have shown gold to be highly active for low temperature CO oxidation reactions when its size is limited to the nanometer scale and dispersed on an oxide support.[5] Au lacks the activity that Pt has for Proton Exchange Membrane (PEM) applications in acidic media. Nevertheless, in alkaline media, Au has been tested to be extremely active and may even surpass the activity of Pt and Pd for several alcohol oxidation reactions [6, 7]. In acidic media, Au is nearly inactive for alcohol electrooxidation due to its weak adsorption capabilities, however, at a high pH, high concentrations of OH⁻ in the electrolyte and adsorbed hydroxyls on Au surface are able to enable the de-protonation of alcohols, and as a result significantly lower the energy barrier for alcohol oxidation reactions[8]. The focus of this investigation is to synthesize a very efficient catalyst for ethanol oxidation in alkaline media with minimal metal loading using a novel electrodeposition technique called Rotating Disk Slurry Electrodeposition (RoDSE) [9].

Alcohols such as methanol, ethanol, and butanol and other oxygenates have been proposed as an alternative liquid fuel on account of the hazards and transportation issues that arise when using H₂ as a primary energy source. The ability to store and produce oxygenates from biofuels make this a highly attractive feed. In addition, simple alcohols provide a higher theoretical and experimental energy density and efficiencies than gaseous fuels [10]. Ethanol is already used as an additive in automotive gasoline (E85), and as a primary fuel has been considered extensively because it is a simple alcohol which can be easily oxidized, can be obtained from biomass, is nontoxic, is a liquid with a high energy density and there is gasoline infrastructure that can be readily adapted for it. Single crystal studies performed on gold electrooxidation have shown that there are two possible mechanisms for base-catalyzed alcohol oxidation on a Au surface: (1) Controlled pK_a alkoxide adsorption [11] and (2) dissociation of β -H on the pre-adsorbed hydroxide on Au surface[6]. However, it is fairly known that there is no catalytic bond breaking involved in the oxidation of ethanol so its main products are acetic acid and acetaldehyde [12].

Although fundamental analysis has been conducted on Au single crystals [12-14], highly dispersed Au catalyst on carbonaceous support for alcohol oxidations needs further insight. It has been found that Au catalytic activity may be equal to or may surpass Pt and for certain reactions due to the lack of poisoning from intermediaries on Au nanoparticles active sites [6]. In addition to carbon support, metal-oxide interactions can lead to the enhancement of catalytic activity by promotion through a bifunctional mechanism where the oxidized metal helps in the complete oxidation of the intermediate species. Moreover, a better hydroxide absorption due to the presence of an oxide species on the catalyst surface may enhance the catalytic activity for oxidation. This implicates the result of a bifunctional mechanism where the adsorption and dissociation of water take place on the oxide, while CO adsorbs on the gold sites located nearby and all the subsequent reactions occur at the metal-oxide interface, as proposed for the water-gas shift reaction.[15-17].

Rare earth oxides may be used as co-catalysts with noble metals to enhance adsorbing and dissociating abilities of the catalyst through the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox cycle. The nature of ceria and the bifunctional mechanism makes the oxide an essential component for low temperature CO oxidation and water-gas shift reaction[17, 18]. To synthesize a metal hybrid between Au and Ce metals, a chelating compound which is widely used for the preparation of catalysts was employed[19]. Ethylenediaminetetraacetic acid (EDTA) can be used as a chelating compound for Ce improving the stability and dispersion of the Ce(III) on the carbon support. Occlusion electrodeposition methods to prepare Pt/CeO_x on glassy carbon electrodes with metal precursor of K₂PtCl₆ and Ce(III) have demonstrated an increase in catalytic activity for methanol oxidation in comparison with the Pt/C system [18]. Furthermore, the activity of the catalyst depends on the Au NPs on the surface of carbon-based support, metal-support interactions, time of electrodeposition and concentrations of Au precursor and carbon based support [20]. An electrochemical technique known as Rotating Disk Slurry Electrode (RoDSE) [9],[21] was used to electrodeposit Au on Vulcan XC-72R and further modified by Ce(III)EDTA impregnation[22],[23] with subsequent electrochemical analysis for ethanol electrooxidation, including surface analysis characterization.

Experimental

Catalyst Preparation

The RoDSE[9],[21] technique for electrodeposition consists of dissolving a metal precursor (AuCl₄; Sigma-Aldrich 99.9 %) in a colloidal carbonaceous support slurry solution. A reduction potential is applied between a RDE glassy carbon working electrode and a reference electrode (Ag/AgCl) at a constant rotating speed to electrodeposit Au onto

the carbon Vulcan XC-72R (Cabot Corporation) substrate. Deposition occurs because the AuNPs are electrochemically reduced when the metal ions come into contact with the surface of the glassy carbon disk electrode and/or when the carbonaceous support at the surface of the electrode is charged and further reduces the Au^{3+} ions into Au^0 .

Deposition of Au nanoparticles on Vulcan consisted on weighing 2.00 mg of the carbon per mL of H_2SO_4 0.100M solution (Fisher, 95-98%) and 8 hours of sonication to increase dispersion of the substrate sites for nanoparticle deposition. The sulfuric acid electrolyte and the hours of sonication are used as an oxidative treatment in order to increase the amount of nucleation sites. Then, 2.00 mL of a 5.00 mM HAuCl_4 in H_2SO_4 metal precursor was added and the solution was stirred vigorously for 2 hours under a nitrogen atmosphere. Electrodeposition of Au was performed at -250 mV vs. Ag/AgCl for eight total hours with the addition of 2.00 mL of precursor every two hours with constant RDE rotation at 1,000 rpm. The electrochemically reduced slurry solution was then filtered and air dried to obtain a powder sample.

Ce(III)EDTA impregnation was conducted on the Au/C after electrodeposition using a method previously developed by Guzmán-Blás et al.[22] Briefly, The Ce(III)-EDTA complex was prepared according to the Ce(III) mass percentage with the desired EDTA. The cerium (III) nitrate (1:1) and EDTA (Sigma-Aldrich, 99.995%) solutions, previously dissolved in 10.00 mL of 18-M Ω -cm deionized water (Barnsted), were mixed and subsequently stirred for 24 hours. The electrodeposited Au/C was dissolved in the Ce(III)-EDTA complex solution and maintained under ultrasonication conditions for 24 hours followed by filtering and dried at 120°C for 24 hours in a conventional oven. The prepared 8% Au/CeO_x/C catalyst was used for electrochemical measurements and physical materials characterization.

To prepare the catalyst ink for electrochemical measurements, 1.00 mg of the powdered catalyst was mixed with Fumion solution (2% w/w) in ethanol. The ink was placed under ultrasonic conditions for 1 hour. Afterwards, the ink was drop casted on a previously polished mirror-like Glassy Carbon Electrode (BAS Inc.). Ag/AgCl (Bas Inc.) and Pt wire were used as a reference and counter electrodes, respectively. All the electrochemical measurements were carried out using a Potentiostat/Galvanostat model 263A EG&G Instruments, Princeton Applied Research.

Catalyst Characterization

X-ray photoelectron spectroscopy (XPS) (PHI 5600ci) was performed with a Mg K α monochromatic X-ray source (350 W) and a hemispherical electron energy analyzer. For XPS, a small amount of the catalytic powder was pressed onto a Carbon tape. The XPS results for the Au 4f binding energy region were analyzed using a curve-fitting program

(Multipack) for peak deconvolution. All the binding energies reported were corrected fixing the carbon peak (C 1s) at 284.5 eV.

X-ray absorption spectroscopy (XAS) was used to determine presence of metals and differences in oxidation states in addition to their respective interatomic distances. X-ray absorption spectroscopy (XAFS) was performed at National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL) using beam line X18A. Au L₃ edge (11918 eV) and Ce L₃ edge (5723 eV) were measured for 20% Commercial Au (Premetek), 9% Au/Vulcan and 8% Au/CeO_x/Vulcan in the transmission mode. The data acquisition setup consisted of three 12 in. ionization chamber detectors: Incidence (I₀) Transmittance (I_T) and reference (I_{Ref}) detector. The gases used in the detectors depended on the element being examined. For Au L₃ edge, 100% N₂ was used in the I₀ chamber while Ar was used in the I_T and I_{Ref} chambers.

Soft X-ray absorption was done at NSLS-BNL beam line U4B while probing the Ce M_{4,5} absorption edges. Total electron yield measurements were performed using the drain current from samples mounted on a conducting manipulator. Energy resolution was ~0.2 eV.

X-ray diffraction (XRD) patterns were generated using a RIGAKU SmartLab diffractometer in reflectance Bragg-Brentano geometry at 40 kV and 44 mA power, equipped with high speed 1D detector (D/teX Ultra). Catalysts morphology was also investigated using a high resolution transmission electron microscope (HRTEM, JEOL, JEM-2200FS). The Au loading was determined by thermogravimetric analysis (TGA) and further confirmed by inductively coupled plasma- atomic emission spectroscopy (ICP-AES, Perkin Elmer 4300I DV). TGA analysis was done in air with a temperature ramp of 10 °C min⁻¹ using a Perkin Elmer STA 6000. Electrochemical characterization techniques, specifically cyclic voltammetry, at 1 and 20 mV/s, and chronoamperometry, for 60 min., were used to evaluate the catalytic activity Au-Ce-EDTA towards ethanol oxidation.

Result and Discussion

The prepared suspension with the carbon support in sulfuric acid for Au electrodeposition is a critical step in order to use the carbon black as an adequate catalyst support by increasing its active oxygen containing functional groups. Sulfuric acid also served as an electrolyte for the dispersion of the Au precursor in the carbon slurry solution. The XPS spectra shown in Fig. 1 was used to evaluate the carbon prior (Vulcan only) and after the oxidative treatment in H₂SO₄ and electrodeposition using the RoDSE technique (9% Au/C). The Vulcan shows both carbon and oxygen peaks however for the 9% Au/C, the O 1s peak is much more pronounced indicating the presence of more oxygen

containing species. These additional functional groups created after the activation treatment are associated to additional oxygen moieties in the substrate which act as adequate nucleation sites to deposit the Au nanoparticles.

Fig. 1. X-Ray Photoelectron Spectroscopy of (a) Vulcan XC-72R after oxidative treatment and electrodeposition of Au (black) and (grey) Vulcan XC-72R without any modification.

X-ray diffraction (XRD) measurements were obtained using a Rigaku Smart Lab III (Cu K α radiation, $\lambda=0.15418$ nm) instrument. Data acquisition consisted on 0.02° step size over 2θ from 30° - 90° . Fig. 2 shows the XRD pattern of RoDSE electrodeposited Au/C with a 9% precious metal loading (9% Au/C), RoDSE electrodeposited 9% Au and Ce promoted (8% Au/CeO $_x$ /C), commercial 20% Au/C (20% Au/C) and the carbon substrate (Vulcan) powder catalysts. Characteristic Au peaks were located at $\theta = 38.1^\circ$, 44.3° , 64.3° , 77.5° and 81.6° which correspond to (111), (200), (220), and (311) lattice plains respectively. The diffraction pattern on the electrodeposited Au catalyst indicated the presence of polycrystalline Au with predominant (111) symmetry evidenced by a sharper peak at 38.1° . Particle size

was approximated to be 26-31 nm for all the catalysts applying the Halder-Wagner method and the Sherrer Equation[24, 25]. There are similarities in terms of the crystal facets and average crystallite size in the electrodeposited materials with the 20% Au/C materials. Moreover, the XRD pattern corroborates that electrodeposition technique via RoDSE method is a viable procedure to synthesize a catalyst out of a metal precursor and depositing it on a carbonaceous support without the need of harsh reducing conditions and/or stabilizing agent. Interestingly, the Ceria peaks do not appear on Fig. 2, hence we believe that the ceria deposited is either amorphous in nature or highly dispersed.

Fig. 2. X-ray diffraction pattern for electrodeposited Au on Vulcan XC-72R, using RoDSE technique, (a) 8 % Au/CeO_x/C (b) 9% Au/C (c) 20% Au/C and (d) Vulcan XC-72R.

Thermogravimetric analysis was conducted in air to determine the amount of Au deposited on the carbon substrate. The analysis consists on a gradual temperature ramp removing the water adsorbed from the sample. Further oxidation of the carbon was followed due to elevated temperatures. From Fig. 3, it can be observed that after reaching 1,000 °C, Au/C remained with a 9.0 %, attributed to the metal loading of the electrodeposited catalyst. With the use of 8.00 mL of 5.00 mM H₂AuCl₄ precursor, the TGA analysis indicated that a loading of 9.0 % was successfully deposited onto carbonaceous support with a 66.0% yield also confirmed by ICP. A higher metal loading could be obtained by adding a higher amount of metal precursor to the sample as shown Fig. 3 were the amount of volume used for

electrodeposition was doubled and an 18.0 % Au loading was obtained, however further characterization was performed on the 9.0 % Au/C. For the Au/CeO_x/C, an 8% Au loading was obtained using ICP for the powdered catalyst.

Fig. 3. Thermogravimetric analysis of RoDSE electrodeposited Au on Vulcan XC-72R. TGA results indicate a metal loading of 9.0% Au/C (—) and 18.0% Au/C (---).

X-ray absorption spectroscopy measurements were performed at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL) using X18B and U4B beam lines. Measurements were carried out at the Au L₃ edge (11,918.7 eV) and Ce M₄ (902.4 eV) and M₅ (883.4 eV) edges. The powder sample data was analyzed using the Athena and Artemis software.[26] Characterization of Au/C electrocatalyst by ex-situ EXAFS can give average information of the coordination geometry in atomic structures of nanoparticles while the Fourier transform of the experimental data can elucidate interatomic distances. The experimental EXAFS data (k^3 weighted, $\Delta k = 2\text{--}14 \text{ \AA}^{-1}$) of RoDSE electrodeposited Au/C are plotted in Fig.1 S1. Fig. 4 (a-b) displays the EXAFS data, which corroborates the behavior of our material compared to commercial Au. There is no significant difference which shows that the chemical environment is very similar to 20% Au/C, with predominantly Au-Au and Au-O/C at approximately $\sim 2.6 \text{ \AA}$ and $\sim 1.5 \text{ \AA}$ – $2.0 \text{ \AA}$, respectively.

In the EXAFS data, at both high Z (Au-Au) and low Z (Au-C) k space, the contributions are mainly of the carbon-supported gold interaction. A k^3 weighted spectra emphasized the high Z contributions in the spectrum.[27] Comparing

the electrodeposited Au with the CeO_x promoted catalyst, Fig. 4(a-b) shows that the Ceria is not perturbing the electron density or coordination geometry of the Au nanoparticles. It is important to note that XAS techniques rely on X-rays as a source so they can penetrate further into the sample so most probably we are observing the bulk electronic behavior of the Au sample, which may not have strong electronic interactions but does not exclude that the process may be occurring at the surface.

Fig. 4. (a) The experimental EXAFS data (k^3 weighted, $\Delta k=2-14$) and (b) Fourier transform (k^3 weighted of $\Delta k=2-14 \text{ \AA}^{-1}$) of (c). 9% Au/C, (—) 8% Au/CeO_x/C, (···) 20% Au/C, (---) and (---) Reference Au foil.

Additionally, NEXAFS experiments conducted at the NSLS beamline U4B helped identify the presence of Ce in its reduced Ce^{3+} form. This is evident by the presence of sharp peaks of Ce^{3+} at 883.8 eV and 902.4 eV, corresponding to the M_5 and M_4 absorption edges, respectively. The oxidized Ce^{4+} would have shown an additional peak corresponding to the same transitions at 886.0 eV and 904.75 eV. However, there is no evidence of their presence indicating that Ce^{3+} ion is the dominant species in the RoDSE electrodeposited 8% Au/CeO_x/C catalyst. This fact is also corroborated by Fig. 5b, showing the characteristic reduced ceria ion for the L_3 transition.

Fig. 5. X-ray absorption spectroscopy of (a) M_4 and M_5 and (b) L_3 absorption edges Au/CeO_x/C. There are two characteristic peaks in the Ce, which correspond to the M_4 and M_5 transition. The L_3 shows the characteristic spectral shape for the Ce^{3+} ion. 8% Au/CeO_x/C, (—) Ce^{3+} standard, (···) with Ce^{4+} standard, (---).

Transmission electron microscopy (TEM) corroborates the formation of Au nanoparticles dispersed in the carbon support with several particle sizes. Fig. 6 shows Au nanoparticles in the 25-30 nm range however there are clumps of Au particles which may also contribute to the features observed in the X-Ray Diffraction pattern which indicated an average crystallite size of 25-30 nm applying the Sherrer equation which is consistent with microscopy results. Interestingly, the Ceria atoms cannot be observed by electron microscopy. As mentioned previously, it seems that CeO_x is highly dispersed as Rolando *et al.* had shown previously.[23] TEM results evaluated for 20% Au/C was show similar dispersion and average nanoparticle sizes but at a higher metal loading. . Hence, the EDTA assisted Ce^{3+} impregnation method likely caused CeO_x deposition on the carbon matrix with a high dispersion since it cannot be observed by XRD or TEM.

Fig. 6. Scanning transmission electron microscopy of Au nanoparticles synthesized by the RoDSE method. (a) Low and (b) high magnification of 9% Au/C (c)-(d) Transmission electron microscopy of 20% Au/C.

Electrochemical Studies

All of the synthesized catalysts were analyzed using cyclic voltammetry (CV). The current was mass normalized for the modified electrode to evaluate all of the catalyst's activity. Normalization by contribution from active surface area of the electrode gives a real indication of the activity of the catalyst, however since the synthesized catalyst's KOH Au oxide stripping peak shown in Fig. 7 have a high capacitance, it introduces errors associated to the estimated charge consumed during the reduction of the Au surface monolayer therefore it was only normalized by the

mass of Au determined using ICP. [28] In a typical Au cyclic voltammetry using KOH as an electrolyte, the Au voltammetry goes into a forward anodic potential and at approximately 0.400 V vs. Ag/AgCl, an oxide layer starts forming at the catalyst's surface. The oxide is then reduced in the reversed backward scan at a potential of 0.100 V vs. Ag/AgCl and the ability for subsequent alcohol oxidation is recovered. Three different catalyst were compared for ethanol electrooxidation: 20% Au/C, 9% Au/C, and 8% Au/CeO_x/C. The amount of Ce in the system was tuned to Au/CeO_x 1:2 ratio based on the highest ethanol oxidation current generated in CV experiments with same parameters. Additional information is given in Figure S2.

Fig. 7. Cyclic Voltammetry of (a) 9% Au/C, (b) 8 % Au/CeO_x/C, (c) 20% Au/C in KOH 0.1 M at 20 mV/s.

Fig. 7 shows the catalyst in 0.100 M KOH. All the catalysts exhibit typical Au voltammetry characteristic. The 9% Au/C and 8% Au/CeO_x/C exhibit a larger contribution from the double-layer current compared to Au 20% due to the lower Au loading which implies a higher loading of carbonaceous which does not participate in the faradaic reaction.

The electrodeposited Au and the oxide promoted metal catalyst share a similar voltammetry since their synthesis methods were similar with the exception of using a chelating agent to impregnate the metal-oxide into the catalyst. Differences in Au loading can be observed qualitatively from the oxide anodic stripping peak where the total area contribution from the peak of 20% Au/C is higher than the electrodeposited catalysts which has 9.0% of Au loading. A higher surface area is also attributed to higher electroactivity since there are more available sites where the oxidation of the alcohol may take place.

Fig. 8 (a) shows the ethanol oxidation voltammetry at a 20 mV/s scan rate. The current density obtained from Table 1 was calculated by subtracting the amount of current generated by the contribution from the capacitive current. Therefore, only the magnitude of the corresponding anodic and reversed cathodic peak was used to show the amount of current density exclusively by the faradaic reaction taking place. Qualitatively, it can be noted that there is a difference in terms of the redox process taking place at the surface of the electrodes. At potentials higher than 0.200 V, the 20% Au/C shows a broad oxidation peak, whereas in the electrodeposited and electrodeposited-oxide-promoted catalyst there is a sharper oxidation peak. The shape of the peaks indicates that the oxidation of ethanol to product intermediates take place in a single step while the Au 20% oxidizes the ethanol but intermediate species are still left at the surface of the catalyst and further oxidation of product intermediary species are taking place at higher potentials. The onset potential was determined by calculating the highest peak in the forward anodic oxidation peak and determining the point where 20% of this I_{Fmax} current was obtained. The electrodeposited Au catalysts share a similar onset potential but when the ceria is present, at the scan rate involved, is affecting slightly the rate of electron transfer in the system. However, the oxidation reaction between the commercially available catalyst and the electrodeposited catalyst shifts towards more negative potentials.

Table 1. Cyclic voltammetry data of the electrocatalytic activity of RoDSE electrodeposited Au on Carbon Vulcan XC-72R after mass and active surface area normalization in 1M EtOH in 0.1M KOH solution. Scan rate of 20 mV/s.

Catalyst	Onset _r (V)	I_{Fmax} (mA mg ⁻¹)	V_{IFmax} (V)
9% Au/C	-0.010	33.9	0.240
8% Au/CeO _x /C	-0.059	36.8	0.250
20% Au/C	-0.010	22.6	0.338

Fig. 8. Cyclic voltammetry in 1M EtOH in 0.1M KOH aqueous solution at (a) 20 mV/s and (b) 1 mV/s of electrodeposited Au on Carbon, 9% Au/C (—), 8% Au/CeO_x/C (···), and 20% Au/C (---).

Fig. 8 (b) shows a linear sweep voltammetry at a scan rate of 1 mV/s to remove most of the capacitive current contribution. At low scan rates the system is allowed to remain at longer period of time at each potential reaching a partial equilibrium state. There is a significant increase in catalytic current from the electrodeposited materials, which leads us to infer that at relatively low scan rates, the catalytic process is significantly favored for the electrodeposited materials and even more favored with the oxide promoted catalyst. Higher current densities at very low scan rates indicate that the catalyst involved has a higher stability towards oxidation of the alcohol during and after the electron transfer. The formation of intermediate species at very low scan rates seem to be poisoning faster the 20% Au/C surface, while the RoDSE electrodeposited material and ceria promoted catalyst have a higher stability towards the oxidation of intermediate species; this would explain the significant difference of the catalyst's behavior at higher scan rates and the substantial decrease of activity at lower scan rates.

Chronoamperometry experiments were performed to determine the stability of the catalyst at oxidizing potentials shown in Fig. 9. The poisoning of the Au catalyst was attributed to the adsorption of product intermediates[12]. It can be noted that at the potential considered, 0.00V vs. Ag/AgCl, the oxidation of EtOH is already taking place. 0.00V was chosen to because all of the catalysts were already oxidizing ethanol at the potentials considered. The results are consistent with LSV measurements conducted at 1 mV/s cyclic voltammograms. The current density gained and stability of the catalyst followed the descending order 8% Au/CeO_x/C > 9% Au/C > 20% Au/C, showing clearly that ceria plays an important role in the electrical transport properties by enhancing the catalyst's stability.

Fig. 9. Chronoamperometry in 1M EtOH in 0.1M KOH solution at 0.00V vs. Ag/AgCl for the electrodeposited Au on Carbon; 9% Au/C (—), 8% Au/CeO_x/C (···), and 20% Au/C (---).

The broader AuOH for Au 20% desorption peak shown in Fig. 3 would lead us to infer that it has a higher surface area and thus a higher electroactivity for alcohol oxidation, however it was not the case. Interestingly, although the electrodeposited catalyst have a lower surface area, their activity is superior to the commercially available catalyst. The electrodeposited materials seem to have a greater electrochemical activity due to the nature of the synthetic process involved. The reducing potential applied modifies the functionalities present on the carbon surface in the form of surface oxides (e.g. carboxylic groups, phenolic groups, lactonic groups, etheric groups) which are responsible for redox properties of the carbon [29]. Since the carbon support is initially sonicated for 8 hours prior to electrodeposition in acidic media, this oxidative environment gave rise to the formation of surface acidic sites on the substrate (Vulcan XC-72R) providing adequate nucleation sites for the anchoring of [AuCl₄]⁻. However, when a reductive potential is applied, some of these oxygen moieties are further reduced and act as a chemical activation, which increases metal dispersion evidenced by their increase in catalytic activity towards ethanol oxidation. XAS data corroborates that

RoDSE electrodeposited Au has essentially the same electronic and chemical environment as the commercial counterpart based on Fig. 4 but the increase in catalytic activity is attributed to the average dispersion and catalytic sites which are formed as a result of the oxidative treatment.

The addition of ceria to the system seems to be taking an effect in the electrocatalysis of ethanol by supplying additional influx of OH⁻ catalytic sites to the redox sensitive system. As previously mentioned, Au catalysis depends on the adsorption of OH in the system and according to Pourbaix diagrams[30], at the potential and pH considered, the cerium is mostly in the form of Ce₂O₃, which on its own, has no catalytic effect in the oxidation of ethanol as shown in Fig. S3. However, we can infer from the electrochemical studies performed that there is an interaction and promotional effect between metal and oxide. Au catalyst performance is limited by the production of intermediates in the system but the addition of OH⁻ in the system from the Ce species seems to be acting as an alternate site for alcohol oxidation therefore granting faster kinetics and increasing the long term stability under an oxidation potential towards alcohol oxidation.

Conclusion

Using the RoDSE technique, we were able to synthesize a Au/C catalyst with a high activity towards alcohol electrooxidation. This technique has the advantages of not requiring a reducing agent and a surfactant to obtain highly active well dispersed nanoparticles. XAS analysis showed that there was essentially negligible difference in terms of electronic structure between the electrodeposited material and the commercially available catalyst, however, the electrodeposited material was significantly more active for alcohol oxidation with lower precious metal loading due to the chemical environment of electrodeposition. Although TEM analysis demonstrates a variety of nanoparticles sizes, there is a significant increase in the activity of the electrodeposited catalyst when compared to the commercial catalyst. In addition, the activity of the catalyst could be greatly enhanced with the addition of a metal/oxide such as Ce³⁺. Hence, the RoDSE method is a powerful tool to obtain particles in the nanometer range but further optimization is needed to obtain a homogeneous distribution of nanoparticle sizes.

Author Information

*Department of Chemistry, Molecular Sciences Research Center, P.O. Box 70377, University of Puerto Rico at Río Piedras, San Juan, PR 00936-8377. E-mail: carlos.cabrera2@upr.edu, Phone: 1-787-523-5319.

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