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Selective electrogenerative oxidation of benzyl alcohol with platinum–graphite packed-bed anodes

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The selective electrogenerative oxidation of benzyl alcohol in 1M sulfuric acid solutions was studied on several types of graphite supported platinum packed-bed anodes in a hybrid continuous-flow cell with an oxygen gas diffusion cathode. Benzaldehyde formed preferentially on all three catalytic packed-beds under electrogenerative conditions ($E_{\mathrm{anode}} < 0.75\,\mathrm{V}$) where the platinum catalyst was not irreversibly oxidized. Tin–palladium chloride graphite-pretreatment before platinum deposition through ethanol reduction significantly enhanced catalytic activity. This electrocatalyst provided current densities as high as $77\,\mathrm{mA\,cm^{-2}}$ (superficial packed-bed cross sectional area) with a platinum loading of 0.89 wt % Pt on graphite at relative low polarization. The origin of the catalytic activity is discussed and evidence is presented on the roles of tin and palladium. Benzyl alcohol oxidation appears to provide a sensitive probe reaction for demonstrating the existence of special types of catalytic centres.

1. Introduction

This investigation is part of a broad effort to extend the application of electrogenerative reactors, wherein the exothermic energy of desired reactions is utilized to generate d.c. current. Recently, much of the work in our laboratories has been directed towards the oxidation of alcohols on graphite supported platinum in liquid phase packed-bed reactors with oxygen cathodes [1–4]. Initially, the electrogenerative oxidation of short chain aliphatic alcohols in aqueous acid solutions was studied to ascertain activity and selectivity for formation of aldehydes and carbocyclic acids or ketones [1]. Here, benzyl alcohol is used as a model aromatic compound for further studies of oxidation and a comparison of three different types of packed-bed anodes. Important considerations in the selection of this substrate were its relatively high solubility in aqueous solutions and well-studied electrochemistry ([5–8] and references therein). Selection of platinum–graphite catalysts was based on promising earlier work (*vide infra*), and possibilities for further development of these types of supported catalysts. Two of the catalysts were synthesized by a platinum chloride ethanol reduction method, differing only in that the graphite for one of the catalysts was pretreated with a tin–palladium chloride solution before the metal deposition [1, 2]. The third catalyst was chosen for its significantly higher platinum surface area relative to the other two catalysts and for its viability in packed-beds with dilute substrate solutions. It was developed earlier in our laboratories, combining some concepts disclosed by McIntyre and Phillips [9] with some of our own technology [10].

In the earlier work, ethanol was found to be an exceptionally effective and convenient reducing agent for platinum deposition on graphite from hexachloroplatinate solutions [1]. Catalysts obtained by this method showed a relatively high degree of selectivity for aldehyde formation from primary alcohols. For ethanol substrate oxidation, the ratio of acetaldehyde to acetic acid was found to be 9 : 1 with the ethanol reduced catalyst, while it was approximately 1 : 1 with a more conventional, hydrogen reduced catalyst [1]. Pretreatment of the graphite with a tin–palladium chloride solution before the platinum reduction step significantly increased both the platinum deposition rate and the ethanol-oxidation with the platinum–graphite anode, although there was some loss in the selectivity for aldehyde formation. Thus, it was of special interest to ascertain the selectivity (as well as activity) with a benzyl alcohol type substrate using some of the previously described catalysts [1, 2]. Advantages of incorporating palladium in the pretreatment relative to tin alone were also demonstrated earlier [2].

The third type of catalyst used in these studies involved an enhanced surface area packed-bed electrode (ESAP) [9, 10]. Generally, graphite particles, used in the packed-beds, have a small surface area relative to other carbons. However, by bonding large surface area carbon-black particles with deposited platinum onto the bulk graphite particles, high areas with large platinum dispersions can be obtained, while still retaining flow (low pressure drop) and electrical resistance advantages of a macroporous graphite structure [10]. Such enhanced surface area packed-bed (ESAP) electrodes significantly improved the effectiveness of the oxidation of dilute sulfur dioxide in sulfuric acid, compared with other platinum-on-graphite packed bed electrodes.

All three catalysts were found to selectively convert

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benzyl alcohol to benzaldehyde, but the Sn/Pd pretreated electrode was distinguished from the other two in that it provided significantly higher current densities with relatively low overpotentials. With particular care for product analyses, selectivity was found to be much greater than with aliphatic alcohols. In contrast to the electrolytic oxidation of benzyl alcohol, which also gave benzoic acid [11, 12], the electrogenerative approach produced only benzaldehyde.

Some of the potential reactions (and calculated E_0 values [13]) of the electrogenerative oxidation of benzyl alcohol under the acidic conditions employed in the cells include:

Anode:

$$C_6H_5CH_2OH \longrightarrow C_6H_5CHO + 2H^+ + 2e^- \quad (0.173\,V) \qquad (1)$$

$$C_6H_5CH_2OH + H_2O \longrightarrow C_6H_5COOH + 4H^+ + 4e^- \quad (0.049\,V) \qquad (2)$$

Cathode:

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O \qquad (1.229\,V) \qquad (3)$$

2. Experimental details

2.1. *Anode catalysts*

The platinum-on-graphite catalysts were prepared as described earlier [1, 2, 10]. Some catalysts from previous experiments, described earlier, were reused with no indication of a decrease in catalytic activity. Acid washed 20–30 mesh graphite (Superior Graphite Desulco 9012) was used as the support for the ethanol reduced catalysts, while the ESAP catalyst was based on a slightly larger 18–20 mesh Desulco graphite support. The freshly prepared tin–palladium chloride solution (0.1 g $PdCl_2$, 30 ml conc. HCl, 5 g $SnCl_2.2H_2O$, and 65 ml H_2O to make 100 ml solution) for pretreatment was allowed to contact the graphite (9.0 g) for one minute before extensive washing with deionized water. This was followed by platinum deposition on the treated graphite particles, using the electroless ethanol chloroplatinic acid reduction method, described earlier [1]. The platinum loading, controlled by the concentration of the chloroplatinic acid solution (0.0025 M; volume 160 ml), was set to 2.0 mg Pt per apparent cross sectional area of the packed-bed, corresponding to about 0.89 wt % Pt (dry graphite packing density = 0.56 g cm^{-3}). For the ESAP electrode, the loading level was 1.0 mg Pt cm^{-2} with hydrazine used as the reducing agent for platinum deposition onto the carbon black [10].

Platinum surface areas for the packed bed particles were measured electrochemically based on the procedure, developed in our laboratory [14], for measuring the charge transferred by hydrogen desorption. A value of 210 μC cm^{-2} of platinum surface coverage was used in the calculation of the surface area.

2.2. *Packed-bed reactor*

The packed bed cell design, reactor operations, electrical equipment and circuitry have been described in detail in previous publications [1, 3]. A schematic of the cell and associated circuitry is provided in Fig. 1. The hybrid electrogenerative cell consists of an anode chamber (51 mm × 13 mm × 4 mm) packed with the supported catalyst (2.6 cm^3) separated from the oxygen gas diffusion cathode compartment (American Cyanamid, LAA-2, 9 mg Pt cm^{-2}) with a cation exchange membrane (RAI Research Corp., RAI 4010). The anolyte feed, containing benzyl alcohol (Aldrich Chemical Co.) at concentrations up to 0.25 M in 1.0 M sulfuric acid, was passed through the packed-bed anode at rates near or above 1 ml min^{-1}. The catholyte, 1.0 M sulfuric acid, held stationary during data collection, was replaced in the time period between successive polarization experiments. The anode potential was monitored relative to a sodium chloride saturated calomel reference electrode (SSCE), attached to the back side of the packed-bed by a Luggin type connector. Data collection for the pretreated electrode was generally stopped, when the anode potential started drifting at higher conversion rates (*vide infra*). For a 0.1 M benzyl alcohol solution at a flow rate near 1 ml min^{-1}, the upper limit of the anode potential was kept below 250 mV vs RHE.

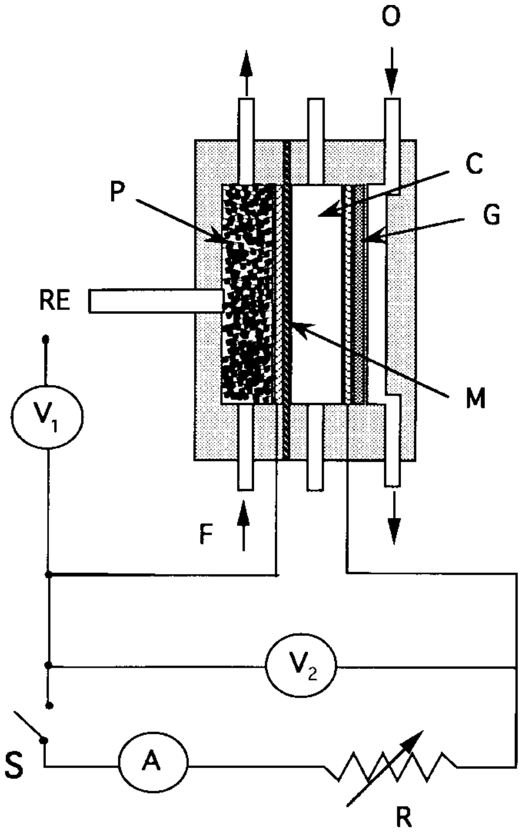

Fig. 1. Schematic of the electrogenerative cell and electronic circuitry. (A) ammeter, (C) cathode electrolyte compartment (4 mm thick), connected to catholyte reservoirs (see reference [3]), (F) anolyte feed, (G) gas diffusion oxygen electrode, (M) cation exchange membrane, (O) oxygen gas inlet, (P) graphite packed bed electrode, (R) variable resistor, (RE) outlet to reference electrode, (S) switch, (V_1, V_2) high impedance voltmeters.

2.3. *Product analysis*

The sensitive nature of the benzaldehyde product towards further oxidation to benzoic acid by atmospheric oxygen necessitated an inert atmosphere for product collection and subsequent sample preparation for high performance liquid chromatography (HPLC) analysis, used in the study of product selectivity. After a 10 min stabilization period at any selected current–voltage setting, the anolyte effluent from the packed bed was collected in a closed three armed flask under flowing nitrogen gas. The acid solution was neutralized with an equivalent of 1.0 M sodium carbonate, and diluted with HPLC grade water by a factor of 3 to 20 times, before 20 μl of the sample was introduced into the column (Econosphere C18 5 μm sphere, length 250 mm, i.d. 4.6 mm). A 50%–50% water–methanol mixture was used for elution and the products were monitored using a Perkin–Elmer diode array (Model LC-235) set at 260 nm. When monitoring for benzoic acid formation, the mobile phase was modified (67% water–33% methanol) to better resolve benzoic acid from the sulfate moiety peaks. The detection limit for benzoic acid was determined to be 1×10^{-5} M in the diluted samples, giving a minimum possible detectable value of the benzoic acid in the anolyte effluent ranging from 5 to 15 mol % of the product (in the worst case). Ether extraction of the effluent on some samples indicated that the possible percentage of benzoic acid formed was far less, generally under one per cent of the product, but the method, as determined by standards, was quite susceptible to benzoic acid formation through air oxidation or from peroxides in the ether. For the aqueous phase analysis, comparisons were made against known standards (Aldrich Chemical Co.) prepared in 0.05 M sodium sulfate solutions. The time interval between collection and analysis was not found to be critical, but most samples were analysed within one day of the experiment.

Analysis of the catholyte for organics migrating through the ion exchange membrane was conducted in a manner similar to that above; however, no protective nitrogen gas blanket over the collection vessel was required for this experiment. The samples were collected for analysis by draining the cathode electrolyte compartment (see Fig. 1) after polarization experiments of almost one hour duration.

3. Results and discussion

Benzyl alcohol in aqueous sulfuric acid solutions was found to be selectively oxidized to benzaldehyde with all of the platinum-on-graphite packed bed anodes studied here under electrogenerative conditions. In the sections below the cell polarization, effect of concentration, and product selectivity are described for the three packed bed catalysts, with emphasis given to the highly effective tin–palladium pretreated electrode. In the final section the tin–palladium pretreatment is considered in somewhat greater detail, and the catalytic enhancement is shown to arise from factors associated with this particular treatment.

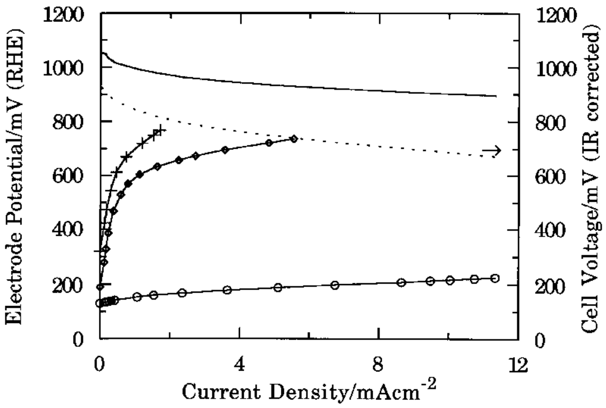

Fig. 2. Anodic polarization curves from various platinum on graphite packed-bed catalysts for oxidation of 0.10 M benzyl alcohol in 1.0 M sulfuric acid: (○) tin–palladium chloride pretreated graphite–ethanol reduced (2.0 mg Pt cm^{-2}), (+) ethanol reduced catalyst (2.0 mg Pt cm^{-2}), and (◇) enhanced-surface-area pack-bed electrode (ESAP) (1.0 mg Pt cm^{-2}). Representative oxygen cathode polarization (solid line). Cell voltage from Sn–Pd pretreated electrode (dotted line), corrected for *IR* loss, $R_{\text{int}} = 0.33\,\Omega$. Anodic flow: 1.0 ml min^{-1} for Sn–Pd pretreated and ESAP electrodes, 1.5 ml min^{-1} for ethanol reduced electrode.

3.1. *Cell polarization*

The performances of the three packed-bed anodes are compared in Fig. 2 for the oxidation of 0.10 M benzyl alcohol in 1.0 M sulfuric acid. The oxygen cathode polarization, also shown, remained unaffected by the changes in the anode packed-bed. The tin–palladium pretreated ethanol-reduced electrode stands out from the ethanol-reduced and ESAP electrodes, both in terms of polarization and temporal stability.

Considering first the pretreated electrode, it can be seen that the overall polarization is rather small. Only a modest 94 mV increase is noted for the current range, compared with a 159 mV decrease for the gas diffusion porous, oxygen cathode over the same

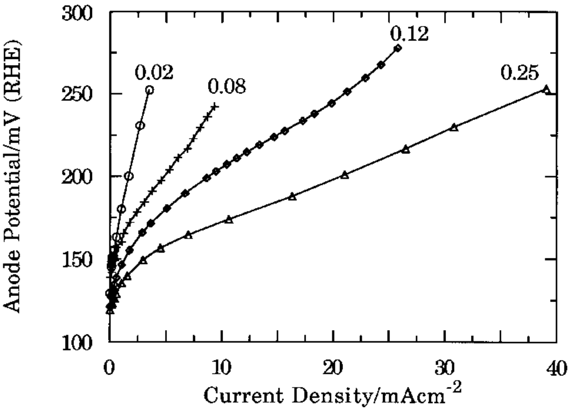

Fig. 3. Effect of varying benzyl alcohol concentration on the anodic polarization curves on the tin–palladium pretreated catalyst (2.0 mg Pt cm^{-2}). Concentrations in moles/litre shown on curves. Anolyte feed varied from 0.83 to 1.2 ml min^{-1}. The per cent conversion of benzyl alcohol to benzaldehyde at the maximum current for each concentration is 31% for 0.02 M, 31% for 0.08 M, 37% for 0.12 M and 34% for 0.25 M.

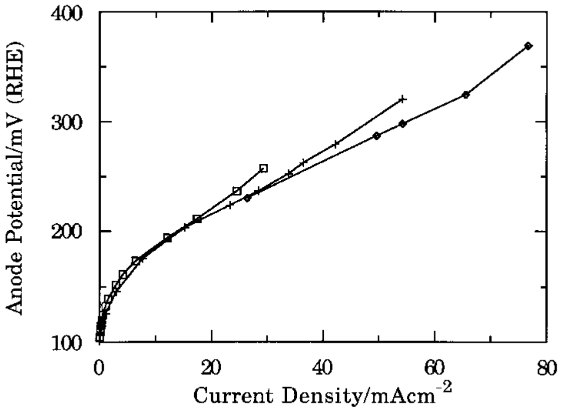

Fig. 4. Dependence of the anodic polarization of the Sn–Pd pretreated electrode (2.0 mg Pt cm^{-2}) upon flow rate of 0.20 M benzyl alcohol in 1.0 M sulfuric acid: (□) 0.84 ml min^{-1}, (+) 2.2 ml min^{-1}, and (◇) 7.9 ml min^{-1}, yielding at maximum current shown, a benzyl alcohol conversion of 35%, 24.6% and 9.7%, respectively.

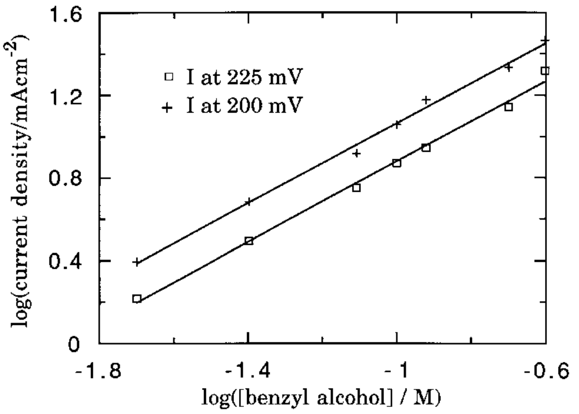

Fig. 5. Plot of log of current density (mA cm^{-2}) against log of concentration of benzyl alcohol (from 0.02 to 0.25M) on Sn–Pd pretreated ethanol reduced electrode at anodic potential of (□) 225 mV and (+) 200 mV in 1.0M sulfuric acid electrolyte. The lines are a linear fit through the respective data sets.

range of current density. This increase can also be contrasted with the other electrode materials, which exhibited anodic polarizations generally greater than 400 mV over a significantly smaller current range. Additionally, the activation overpotential, often a prominent feature, is relatively insignificant, all indications of facile electrode kinetics. At higher currents, the polarization increase appears almost linear with the polarization voltage, with a slope that is concentration dependent (see Figs 3 and 4). At benzyl alcohol to benzaldehyde conversion rates exceeding roughly 20%, the polarization deviates positively from the linear. Increased anolyte flow eliminated the upward curvature and restored the more linear response, suggestive of a mass transport influence (as shown in Fig. 4 for 0.20 M benzyl alcohol at various flow rates). If the cell was operated too far into the nonlinear regime at the higher conversion rates, further increases in polarization (i.e. loss of stability) and irreversible catalyst deactivation was noted at potentials as low as 240 mV vs RHE. Such behaviour is reminiscent of the anodic oxidation of propane on platinum electrodes in acid electrolytes at lower temperatures, although the potential range of this type of deactivation lies above 500 mV [15, 16]. Otherwise, the data were reproducible over the course of several hours of cell operation. Varying the flow rate (~0.8 to over 3 ml min^{-1}) only modestly affected the polarization curves except at the lowest benzyl alcohol concentration (0.01 M) and at conversion rates sufficient to cause transport related effects.

Much greater current densities could be achieved, provided instability difficulties were ameliorated through higher benzyl alcohol concentrations and faster anolyte flow rates. Current densities as high as 77 mA cm^{-2} at an anode potential of 369 mV vs RHE (*IR*-corrected cell voltage, 272 mV) were achieved with 0.20 M benzyl alcohol at a flow rate of 7.9 ml min^{-1} (see Fig. 4). At an alcohol concentration of 0.25M even higher values up to 90 mA cm^{-2} at 7.4 ml min^{-1} were obtained ($V_{\text{anode}} = 320$ mV; $V_{\text{cell}} = 300$ mV); however, phase separation of the more insoluble benzaldehyde product also occurred at this concentration. Benzaldehyde was found on the cell walls after the experiment, and correspondingly, the current accountability of the product in the effluent was under 60%. The solubility limit of benzyl alcohol in 1.0M sulfuric acid at room temperature was determined to be approximately 0.28 M.

A strong concentration dependence of the polarization curves with the benzyl alcohol concentration is noted in Fig. 3. A plot of the log of current density against log of concentration at constant potential yielded a straight line with a slope of one (see Fig. 5), indicating a first order dependence with respect to benzyl alcohol over the investigated concentration range. Modification of the electrolyte concentration from the usual 1.0 to 0.1 M sulfuric acid did not appear to influence the polarization curve, and a small initial concentration of benzaldehyde (0.014M) in the anolyte feed (0.10 M benzyl alcohol), produced at most a minimal polarization increase (20 mV at 8 mA cm^{-2}). Log of current against anodic potential plots did not exhibit a clearly defined Tafel region for the polarization data. These results contrast with those obtained from the other two catalysts (*vide infra*). The exchange current density was estimated to be around 2×10^{-6} A cm^{-2} for 0.1 M benzyl alcohol, using a linear approximation of the polarization data at small overpotential near the open circuit voltage (125 to 130 mV vs RHE) [17] and the platinum surface area given in Table 1.

A distinctly different response from the above was observed for the ESAP electrode and the ethanol reduced platinum graphite electrode without pretreatment (see Fig. 1). The strong polarization of both electrodes and significantly higher open circuit voltages (usually over 250 mV for 0.1 M benzyl alcohol) are the most striking differences. The similarity of the two catalysts in terms of the polarization response and stability (*vide infra*), supports grouping these catalysts together. At low currents (under 1 mA cm^{-2}) both electrodes strongly polarized, indicating slow kinetics. The much larger polarization limited the

Table 1. Platinum surface areas of the packed bed electrodes

Catalyst	*Pt loading* /mg Pt cm^{-2}	*Pt area** /cm^2 Pt app. cm^{-2}	*Pt dispersion*§ /%
Tin–palladium pretreated/ethanol reduced	2.0	400	8.5
Ethanol reduced	2.0	290	6.2
ESAP	1.0	1000†	43

* Area of Pt surface per geometrical cross-sectional area for the packed bed (6.45 cm^2).
† Area estimated by comparison to other measured samples of like loading and preparation.
§ Dispersion or per cent platinum exposed calculated from the ratio of measured platinum surface area to the bulk platinum surface area of 2356 cm^2 per mg Pt [25].

possible currents to only a fraction obtained from the pretreated catalytic electrode. Data collection at anode potentials above 750 mV was avoided, since previous experience showed that irreversible deactivation tended to occur at these potentials, presumably because of irreversible oxidation of the platinum catalyst [1, 3]. Both catalysts also exhibited an inherent instability towards benzyl alcohol oxidation not observed with the pretreated electrode, as reflected by unreproducible polarization curves. After several polarization experiments, the changes were smaller in magnitude, reflecting a possible conditioning effect. Shifts to higher voltages were particularly severe at current densities below 1 mA cm^{-2}. Unlike the pretreated electrode, increasing the anolyte flow (over 1 ml min^{-1}) did not appear to improve the response either in terms of performance or stability; however, of the two catalysts, the ESAP was the more stable.

The two electrodes differed in response to variations in the substrate concentration. The polarization curves from the ESAP electrode were only weakly correlated with the benzyl alcohol concentration in the range from 0.01 to 0.20 M, while the ethanol reduced electrode showed a much stronger dependence, but determination of the reaction order was not feasible because of instability difficulties. Conversion rates of benzyl alcohol to benzaldehyde for the ESAP electrode were as high as 25% (0.01 M benzyl alcohol) with no indication of a transport related stability problem, indicating the usefulness of the enhanced surface area structures, particularly at low concentrations.

Unlike the data from the pretreated electrode, log of current against anode potential plots (from data taken after several polarization curves) were linear for both electrodes throughout the entire current range with Tafel slopes in excess of 230 mV (decade)$^{-1}$ of current. High Tafel slopes of this magnitude (230 to 260 mV (decade)$^{-1}$ under 1.4 V) were also reported for electrolysis of benzyl alcohol in 0.5 M sulfuric acid with ruthenium oxide electrodes [18]; these can be compared to a much lower value of 120 mV (decade)$^{-1}$ with platinum electrodes in acetonitrile [7]. High Tafel slopes for organic reactions are not exceptional and have been interpreted in terms of adsorption of organic molecules on the electrode surface [19]. Testing of the ESAP electrode with a small initial concentration of benzaldehyde in the anolyte feed does provide some understanding of the high values for the Tafel slope. Unlike the results for the pretreated electrode, addition of 0.011 M benzaldehyde with 0.10 M benzyl alcohol greatly inhibited the electrogenerative oxidation, causing a substantial increase in the polarization. The new polarization curve exhibited a Tafel slope of 140 mV (decade)$^{-1}$, suggesting that electrogeneratively produced benzaldehyde (product interference) may be a contributing factor in the polarization response of these electrodes. Exchange current densities were derived from the log of current against potential plots, using the true platinum area (Table 1) and calculated E_0 (173 mV, Equation 1) for the formation of benzaldehyde. The values for i_0 were approximately the same for the two catalysts, around 6×10^{-8} A cm^{-2}, implying the different activities to be the result of the surface area variation, and further supporting the grouping of these catalysts together.

The oxygen gas-diffusion cathode functioned as the counter electrode in the experiments and was not the subject of study. Generally, the cathodic polarization curves were reproducible to within 15 mV or less. As indicated in earlier work with the aliphatic alcohols [1], the cation exchange membrane is not completely impermeable to organic substrate materials. This can lead to a buildup of organic species in the catholyte during the course of a polarization experiment. It was concern for this possibility that led to a cell design with provisions for periodically changing the cathode electrolyte [3]. At the end of one polarization experiment of almost one hour duration, the concentrations of benzyl alcohol and benzaldehyde were found to have reached values as high as 0.02 and 0.001 M, respectively. Some loss of catalytic activity of the cathode was evidenced by a roughly 40 mV drop in the open circuit voltage, if the electrolyte was not changed. The effect was not permanent and replacement of the catholyte after the polarization experiment (approximately every hour) restored the open circuit voltage to consistent values.

3.2. *Product selectivity*

The electrogenerative oxidation of benzyl alcohol on platinum-on-graphite packed bed reactors is highly selective, forming only benzaldehyde for the catalysts with the operating conditions studied here. The final concentrations of benzaldehyde and benzyl alcohol were monitored in the anolyte effluent, and the accountability of the currents was near (100 ± 20)%

for both the reactant and product. Greater variation occurred with samples collected at low currents. The current accountabilities tended to be slightly high for the aldehyde (average 107%), and possibly reflect some experimental difficulties associated with minor changes in the effluent flow rate when applying a stream of an inert gas over the collection vessel, which was exposed to the atmosphere (*vide supra*). The high selectivity was maintained even with dilute solutions and conversion rates of 25%, where further oxidation to benzoic acid might be expected to occur. No detectable benzoic acid was found (detection limit is roughly 5 mol %; *vide supra*) in any of the samples tested, provided protection from air oxidation was maintained. When air oxidation occurred with some samples, the concentrations of benzaldehyde decreased and benzoic acid could be detected.

The high selectivity of the electrogenerative approach is a consequence of the low anode packed bed potential limit set by the reaction *per se*. This is in contrast to electrolysis, which operates at higher potentials, imposed by an external source. Generally, direct electrolysis of benzyl alcohol solutions with bulk platinum electrodes yields a mixture of the aldehyde and carboxylic acid [11, 12], except at low controlled potentials, where benzaldehyde can form preferentially. Such low voltage conditions with significant currents and selectivity for packed-bed catalytic electrodes are achieved here through electrogenerative operation in aqueous systems.

Various approaches, used previously by other workers in the electrolysis of benzyl alcohol, provide some insight into understanding the selectivity. In direct electrolysis with batch type reactors, acidic conditions (comparable to those used here) are generally avoided because of polymerization [20]; consequently, basic solutions are most frequently employed, often in the presence of nonaqueous solvents [7, 8]. Miller and coworkers reported a product yield of 30% benzaldehyde and 40% benzoic acid for the direct electrolysis of benzyl alcohol on platinum electrodes in acetonitrile with $LiClO_4$ at 1.9 V ($Ag | 0.1\ M\ AgNO_3$) [12]. The yield or selectivity can be improved by electrode modification (or replacement) or by use of a mediated system, many of which are two-phased and require a phase transfer catalyst [20–23]. Most of these approaches preferentially yield benzaldehyde, but nickel oxides (and related electrodes) greatly favour benzoic acid [23]. The key to the selective production of benzaldehyde in the indirect electrolytic systems appears to be the use of a relatively mild oxidizing agent [24]. Often employed mediators, such as hypobromite, ruthenate (RuO_4^{2-}), or triarylamine cationic radicals are not particularly strong oxidizing agents, and can be formed at potentials lower than that typically required for direct oxidation. In like manner, several studies have also shown that selective oxidation is also possible through potential control [5, 20]. Weaver and coworkers, using a potential step FTIR spectroscopy technique, reported benzaldehyde formation on a polished polycrystalline \downarrow platinum electrode in 0.1 M perchloric acid at an anode potential range between approximately 0.6 and 1 V vs RHE [5]. Only when the potential was above one volt was benzoic acid formed.

The high selectivity of the electrogenerative cell here as well as the mediated systems above for the oxidation of benzyl alcohol appear to be a consequence of operating below the threshold potential for benzoic acid formation. In the electrogenerative reactor employed for our experiments, the potential of the packed-bed anode did not exceed 0.75 V. The Sn/Pd pretreated platinum-on-graphite catalysts are notably more catalytic than bulk platinum electrodes, since significant amounts of benzaldehyde were produced at substantially lower potentials.

On a practical level compared to electrolysis, the electrogenerative process provides a simple, and highly efficient method for selectively oxidizing benzyl alcohol and related aromatic materials without a power supply and control equipment.

3.3. *Tin–palladium chloride pretreatment*

The steady-state polarization measurements segregate the packed-bed catalysts into two groups, based on their properties, with differences apparently arising from the deposition procedures. The tin–palladium pretreated ethanol-reduced catalyst exhibited high current densities at low polarization with excellent temporal stability and nonlinear log of current against potential plots. On the other hand, the ESAP and ethanol-reduced materials showed high overpotentials at low currents with poor stability over short periods of time and high, linear Tafel slopes. The distinguishing factor (between the two groups) is the pretreatment step (compare ethanol reduced materials).

In investigating some of the factors that might be mechanistically important in causing the differences, a graphite sample, pretreated with the Sn/Pd solution without any platinum deposition, was tested, and found to exhibit no activity towards benzyl alcohol oxidation. It can be surmised that platinum, as an active catalyst, works in conjunction with or is at least altered by the pretreatment components. In the preparation of platinum-on-graphite catalyst, one important role of the pretreatment step is to catalyse the platinum deposition while simultaneously enhancing the efficiency of the deposition process (any residual platinum in solution is reduced from several per cent to near zero) [2]. Deposition time is reduced from 90 min to 10 min. These improvements are apparently a result of a modification of the graphite surface, presumably through colloidal tin–palladium deposits [2]. The second effect of the pretreatment involves an interaction with the platinum to alter its catalytic activity either as it is being deposited or afterward. On the basis of previous work [1, 2], the platinum surface area, its crystallographic morphology, or platinum-surface activator (Sn/Pd) interactions could be important factors in the enhancement. These are considered below.

The active surface area of an electrocatalyst can be an important parameter, and should be considered in the comparison of the apparent activity of different catalysts. Surface areas are shown in Table 1 for each catalyst along with platinum loading level and per cent platinum dispersion. The two ethanol reduced catalysts here have approximately the same surface area; thus, area is not a determining factor in accounting for the superiority of the pretreated catalyst. However, some correlation does exist between the surface areas of the ESAP and ethanol reduced catalysts with their catalytic activities (compare Fig. 1 with Table 1).

In distinguishing between the crystallographic or platinum–Sn/Pd interactions as the important factor, an ethanol-reduced graphite supported platinum catalyst, previously used for benzyl oxidation, was treated with the tin–palladium solution and tested again. Figure 6 shows the anodic polarization curves before and after the treatment. The large improvement in current, lowering of the open circuit voltage, smaller activation overpotential and subsequent shallow almost linear increase in the polarization are all properties associated with the pretreated catalyst. Moreover, the catalyst now exhibited an increased stability; after an initial conditioning, the polarization curves were reproducible. Thus, the enhancement involves a synergistic interaction between platinum and a residue from the tin–palladium treatment. Since the post tin–palladium treatment would not have been expected to induce any significant crystallographic changes, it can be concluded that effects relating to possible changes in the platinum morphology are minor. Improvements in catalytic activity by tin–platinum interactions are well-known phenomena, observed in methanol fuel cell oxidations [2, 26, 27]. The general similarities, notwithstanding, the enhancements observed for the two reactions may not be mechanistically related. The effect observed for methanol oxidation has sometimes been interpreted in terms of tin acting as a co-catalyst by providing the oxygen atom required for the formation of CO_2 from an adsorbed CO intermediate [27, 28]. However, no oxygen transfer is necessary in the bulk oxidation of benzyl alcohol to benzaldehyde, implying that the tin–palladium–platinum synergism may be of a different nature.

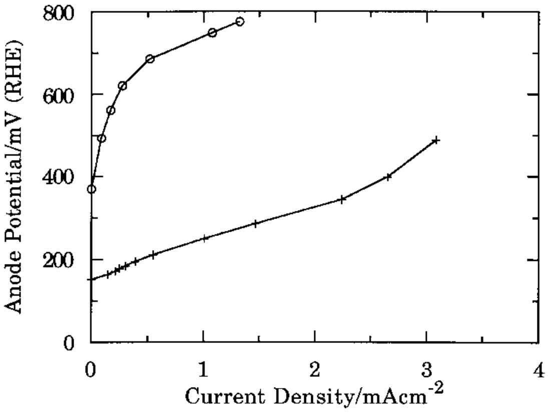

Fig. 6. Effect of post tin–palladium treatment on ethanol reduced catalyst (2.0 mg Pt cm^{-2}) on 0.10 M benzyl alcohol: (○) before treatment (anolyte flow 1.3 ml min^{-1}), (+) after treatment (anolyte flow 1.0 ml min^{-1}).

From the results above and previous studies [2, 27, 28], it appears that the enhancement of catalytic activity for oxidation of organic alcohols results from the presence of all three metals, platinum, tin, and palladium at catalytic centres. Palladium appears to have little activity for organic dissociative processes in the electrochemical potential regions of interest here [5, 29], but it does enhance the effect of the tin addition possibly through stabilization of small tin aggregates in contact with platinum, as indicated from additional experiments. A platinum-on-graphite catalyst prepared with a $SnCl_2$–HCl pretreatment exhibited substantial catalytic activity, which was somewhat comparable to the tin–palladium pretreated catalyst, but without the long-term stability. The open circuit potentials for both pretreatments were about the same (130 mV for 0.1 M benzyl alcohol), while at a current of 8 mA cm^{-2} the anode potential for the Sn-pretreated electrode was 300 mV compared with 200 mV for the Sn/Pd pretreated catalyst.

For the oxidation reaction of interest here the tin–palladium pretreatment enhances oxidation through multiple effects including, perhaps, greater adherence of catalyst to the graphite surface [2]. However on the basis of what has been uncovered to date, the improvement in catalytic activity results from the facilitated removal of either inhibiting CO, arising from side reactions of benzyl alcohol oxidation, or the ϕC*HOH adsorbed intermediate from the region of catalytic centres. Some view the tin role as broadly promoting the activation of water

$$H_2O \longrightarrow {}^*OH + H^+ + e^- \tag{4}$$

to provide adsorbed hydroxyl radicals [28]. There are also many other explanations most recently reviewed by Iwasita-Vielstich, and Haner and Ross [27, 30]. The view put forth by Iwasita-Vielstich, involving adsorbed Sn^{2+} and variations thereof, including the incorporation of minor amounts of palladium here, permits a rationalization of the mechanism of activation. In this formulation, Sn^{2+}, acting as a ligand, donates σ-electrons through a lone pair to platinum, while the d-orbitals become possible π-electron acceptors. Species II in Reaction 5, below, or a related intermediate can either donate an oxygen to produce a hydrogen ion or accept hydrogen as shown below in Equations 6 and 7.

$$\underset{\text{(I)}}{(Pt)[Pd]Sn^{2+}_{ads}} + H_2O \Longleftrightarrow \underset{\text{(II)}}{(Pt)[Pd]Sn(OH)^{+}_{ads}} + H^+ \tag{5}$$

followed by

$$\begin{aligned}(Pt)[Pd]Sn(OH)^{+}_{ads} + (Pt)CO &\longrightarrow CO_2\\ &+ (Pt)[Pd]Sn^{2+}_{ads} + H^+ + 2e^-\end{aligned} \tag{6}$$

where adsorbed CO might be involved or

$$(\mathrm{Pt})[\mathrm{Pd}]\mathrm{Sn(OH)}^{+}_{\mathrm{ads}} + (\mathrm{Pt})\mathrm{C_6H_5C^{*}HOH} \longrightarrow \mathrm{C_6H_5CHO} + (\mathrm{Pt})[\mathrm{Pd}]\mathrm{Sn}^{2+}_{\mathrm{ads}} + \mathrm{H_2O} + 1\mathrm{e}^{-} \quad (7)$$

where adsorbed radical intermediate may be inhibiting the reaction. [Pd] is incorporated in the formula to represent minor amounts of palladium associated with the tin aggregate, which presumably stabilizes this catalyst on the platinum. Reactions 6 and 7 provide a formalism for explaining what takes place. Other intermediates equivalent to I and II might be formulated [31, 32]. Without palladium a pretreated catalyst, involving tin alone, studied in our laboratories, gradually lost activity as polarization experiments were repeated. This is similar to the experience of others, where activity is reported to decrease with the leaching of Sn [26].

In any event the tin–palladium treatment has been demonstrated to be of substantial benefit in improving the catalytic efficiency of platinum-on-graphite electrodes for the oxidation of benzyl alcohol. There is good evidence that platinum–tin–palladium catalytic centres are involved. In earlier work from our laboratories, a similar, but less dramatic enhancement, was observed for several aliphatic alcohols (ethanol, 2-propanol, and methanol) [2]. Thus, this type of treatment with the resulting catalytic centres and related ones are of value in enhancing catalytic activity for oxidation, opening possibilities for more improvement and even wider applications. Further development of the catalysts, resulting from the deposition processes, might increase the single pass conversion rate. The benzyl alcohol oxidation also appears to be a good probe reaction for indicating the existence of a new type of stable, efficacious centre for oxidation. The type of tin–palladium treatment, described here and earlier, broadens the potential scope for electrogenerative processing for the future. It also may be useful for preparation of electrocatalysts for conventional electrolysis reactions and for heterogeneous catalysts.

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