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# Electrochemical sulphur dioxide oxidation with platinum–aluminum electrocatalysts

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Platinum–aluminum electrocatalysts supported on carbon black were investigated for electrogenerative sulfur dioxide ($SO_2$) oxidation in hybrid type, liquid-phase $SO_2/O_2$ cells. Incorporation of aluminum with platinum electrocatalysts on carbon resulted in an electrocatalytic activity increase for $SO_2$ oxidation over the whole investigated range (1–30 at % aluminum). Significant synergistic effect from aluminum was observed when even a small amount, as little as 1 at %, was incorporated in the platinum. A maximum 68% improvement was obtained when 10 at % aluminum was incorporated in the platinum. Results of an ESCA study and electrochemical platinum surface area measurement supported the hypothesis of an electronic interaction between platinum and aluminum.

## 1. Introduction

The anodic oxidation of sulfur dioxide ($SO_2$) can be involved in several electrochemical processes associated with energy conversion cycles [1–5]. For this reaction to be useful, it is necessary to use electrocatalysts which can increase the reaction rate with low electrode overpotentials. This reaction, although thermodynamically favourable, does not by itself occur at a significant rate because of poor kinetics [6]. Platinum has been a favoured electrocatalyst because of its high electrocatalytic activity and inert character.

In several electrochemical studies, bulk metals such as platinum [7–11], gold [7, 11–14], graphite [15], activated carbon [16], and lead [17] have been investigated for $SO_2$ oxidation in aqueous sulfuric acid solutions. In terms of practical catalyst development, the work by Appleby and Pichon [7] is noteworthy. They investigated electrocatalysts for $SO_2$ oxidation in the $H_2SO_4$–$SO_2$ thermoelectrochemical cycle. Adsorbing metals (e.g., platinum) had electrocatalytic activities similar to those of nonadsorbing metals (e.g., gold). Rhodium was superior to platinum in 2 N $H_2SO_4$ containing $10^{-3}$ N $SO_2$, but the electrocatalytic activity of rhodium declined with time as metal surfaces became oxidized. Ruthenium and iridium were less active than platinum. Their low electrocatalytic activities were attributed to a greater tendency to oxidize. Carbon, graphites, and carbides (TiC, WC) also were slightly active.

Although the studies above were done with bulk metal electrodes, there have been others [1, 2, 18–22] with supported metal electrodes. Wiesener *et al.* [1, 21, 22] investigated electrocatalysts of vanadium(V) and aluminium(III) oxides with traces of platinum on porous carbon supports. Their electrocatalytic activity was as much as 30% higher than pure platinum. Aluminium(III) oxide was incorporated to increase vanadium(V) oxide stability in aqeuous sulfuric acid solutions.

Lu and Ammon [2] investigated three different types of electrodes: smooth bulk metal electrodes, gas diffusion-type carbon-supported metal electrodes, and titanium screen-supported metal electrodes. Platinum, palladium, gold, ruthenium, renium, iridium, rhodium, and their oxides were tested in 50 wt % $H_2SO_4$. Of these, palladium and palladium oxides showed the highest electrocatalytic activities for $SO_2$ oxidation. $RuO_x$–$TiO_2$/Ti and $IrO_x$–$TiO_2$/Ti were inactive.

Langer *et al.* [18, 20] investigated graphite sheet-supported platinum electrodes for $SO_2$ oxidation and developed an *in situ* sulfur activation procedure for enhancing platinum electrocatalytic activity. Controlled electroreduced sulfur layers on platinum surfaces produced a significant increase in electrocatalytic activity for $SO_2$ oxidation. In view of the sulfur activation effects on platinum surfaces [20], it became of interest to determine if combining platinum with other metals could further improve the original platinum electrocatalytic activity. This type of modification might produce even more favourable interaction between sulfur-modified platinum electrocatalyst surfaces and adsorbate bonds in $SO_2$ oxidation. Although complete alloying of platinum with the second metal component might be preferred in this situation, an electrocatalytic

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activity enhancement also might result for supported bimetallic electrocatalysts that do not form alloys in the bulk phase.

In testing this type of electrocatalyst modification, titanium, vanadium, chromium, manganese, iron, cobalt, copper, palladium, and aluminum were incorporated into highly dispersed platinum crystallites supported on carbon blacks in our laboratory [21–26]. To obtain intimate mixing between platinum and the second metal component by heat treatment at ca. 1000°C, the preferred metals were those having relatively low melting points. After screening experiments with platinum bimetallic electrocatalysts with 5 at % of the second metal component, platinum–aluminium electrocatalysts were chosen for investigation in detail for electrogenerative $SO_2$ oxidation activity. These carbon black-supported platinum–aluminium electrocatalysts were prepared in the form of enhanced surface area packed bed (ESAP) electrodes [27], so that the electrocatalysts could be tested in a convenient packed bed anode with a flow-through electrolyte while enhancing mass transfer processes.

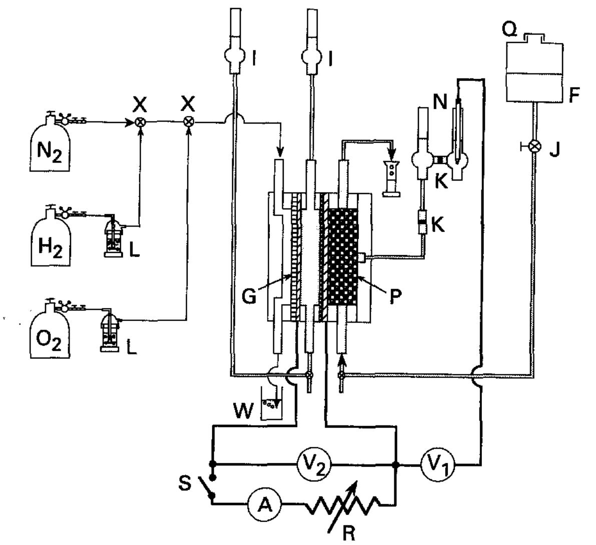

Fig. 1. Schematic representation of an experimental setup: (A) ammeter, (F) feed, (G) gas diffusion electrode, (I) catholyte reservoir, (J) valve with PTFE plug, (K) fine glass frit, (L) gas sparger with water, (P) packed bed electrode, (N) NaCl-saturated calomel electrode, ($V_1$, $V_2$) high impedance voltmeter, (Q) glass cap, (R) variable resistor, (S) switch, (W) beaker with water and (X) three-way valve.

## 2. Experimental details

### 2.1. *Electrode preparation*

Carbon black-supported platinum electrocatalysts (E-Tek, Inc., 10 wt % Pt on Vulcan XC-72R, 0.5 g) were ultrasonically dispersed in 15 ml of deionized water for 5 min. The appropriate amount of aluminium salts (Aldrich Chemical Company, $Al(NO_3)_3 \cdot 9H_2O$, 98%, ACS reagent) dissolved in 2 ml of deionized water were then added to the dispersion followed by mixing completely with a magnetic stirrer. The dispersion was further mixed under moderate heating for ca. 1 h for removal of visible solutions. The catalyst then was dried at 140 °C in an oven for 2 h. For agglomeration of platinum and aluminum crystallites, the catalyst was then heat-treated at 930 °C for 1 h under argon flow in a tube furnace. The heating and cooling temperature speeds were adjusted to ca. 50 °C min$^{-1}$.

The prepared electrocatalyst was then fabricated and tested in the form of enhanced surface area packed bed (ESAP) electrodes. With this approach, the high surface area Vulcan XC-72R-supported electrocatalysts were attached to larger coarser graphite particle supports for packed bed operation. Detailed procedures for fabrication of ESAP type electrodes have been described [27]. Through use of a particular fabrication technique, it is possible to test the Vulcan XC-72R-supported electrocatalysts in a completely drenched mode while minimizing mass transfer limitations by flowing electrolyte through the packed bed.

### 2.2. *Cell polarization experiments*

The electrocatalysts were tested in a hybrid sandwich type, liquid phase electrogenerative $SO_2/O_2$ cell of the type shown in Fig. 1. This cell incorporates an ESAP anode with a gas diffusion-type oxygen cathode (American Cyanamid, LAA-2, 9 mg Pt black cm$^{-2}$). The anode and the cathode were separated by both electrolyte (3 M $H_2SO_4$) and a cationic exchange membrane (RAI Research Corp., R4010). The membrane was used to hinder oxygen cathode poisoning through dissolved $SO_2$ transfer from the anode compartment and to avoid ‘chemical shorting’ in the electrogenerative cell.

Before cell polarization experiments, the anode was electrochemically pretreated in argon-purged 3 M $H_2SO_4$ to assure reproducible results by oxide removal through reduction pretreatment. The anode potential was maintained at 0 mV vs RHE for 30 min using a constant current power supply during which time hydrogen gas was fed to the cathode gas chamber maintained. After this, the internal resistance (IR) of the cell was measured with a micro-ohmmeter (Keithley Instruments, model 580). Careful electrode pretreatment resulted in a minimum internal cell resistance and reproducible cell polarization behaviour. After the resistance measurement, the cathode gas chamber was purged with nitrogen, followed by excess oxygen feed. To remove any residual hydrogen remaining in the ESAP anode pores from the electrochemical reduction pretreatment, a current of 10 mA was drawn from the cell through adjustment of an external variable resistor until the anode potential rose above 250 mV vs RHE. Then the $SO_2$-containing sulfuric acid solution was introduced to the anode. Polarization curves were obtained by decreasing the external resistor load from open circuit. After the first polarization run, the anode was activated by *in situ* sulfur treatment [20] to obtain maximum electrocatalytic activity of this electrode for $SO_2$ oxidation.

## 3. Results and discussion

### 3.1. *Performance of platinum–aluminum electrocatalyst for $SO_2$ oxidation*

The performance of the platinum–aluminium electrocatalyst (10 at % Al) in electrogenerative $SO_2/O_2$ cells is illustrated in Figs 2 and 3 for a platinum loading of 1.0 mg Pt $cm^{-2}$. Three molar aqueous sulfuric acid electrolyte was selected because it fell in the range of best performance at room temperature. High $SO_2$ concentration in the anolyte assured that cell performance was studied under kinetically-limiting conditions with minimal concentration polarization effects. However, $SO_2$ concentration was limited to a 0.9 M maximum to minimize $SO_2$ gas bubble formation complications which can occur in the anode compartment.

As can be seen from Fig. 2, with the platinum–aluminium electrocatalyst in $SO_2/O_2$ cells, a current density of 165 mA $cm^{-2}$ was achieved. This is equivalent to a calculated $SO_2$ oxidation rate of $6.0 \times 10^{-6}$ g mol $SO_2$ $s^{-1}$ in the 2 $cm^3$ packed bed (50.8 mm × 12.7 mm × 3.2 mm), based on an earlier study of quantitative aspects of the oxidation [20]. The performance of the platinum–aluminium electrocatalyst anode was significantly better than that of pure platinum electrocatalyst as can be seen from Fig. 3. Its superior capacity for electrogeneratively oxidizing $SO_2$ was demonstrated by the fact that it generated twice the current of the pure platinum electrocatalyst at the anode potential of 500 mV vs RHE.

### 3.2. *Effect of aluminium composition on anode performance*

To investigate the activities of platinum–aluminium electrocatalysts as a function of platinum and aluminium composition, aluminium content was varied in the range of 0–30 at % based on platinum. By keeping the platinum amount constant in all of these electrocatalysts, activities could be directly compared. Results are shown in Fig. 4. Maximum 68% improvement was obtained with 10 at % aluminium incorporated in the Vulcan XC-72R-supported platinum electrocatalyst. The importance of this effect can be demonstrated by the fact that even 1 at % aluminium addition increased the original platinum electrocatalytic activity as much as 35%. Above 10 at % aluminium, the electrocatalytic activity decreased and remained at about a 50% improvement level.

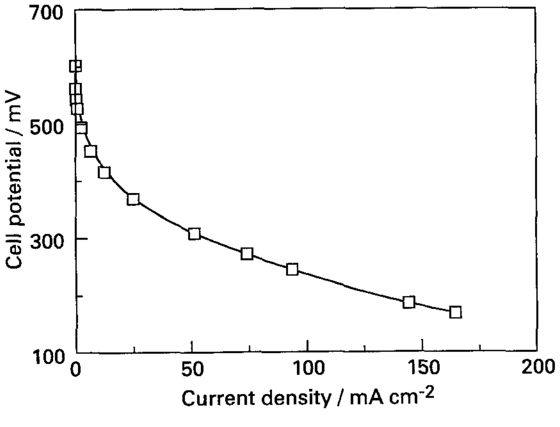

Fig. 2. Performance curve for an electrogenerative $SO_2/O_2$ cell. Anode: ESAP electrode (1 mg Pt $cm^{-2}$, 10 at % Al); cathode: LAA-2; Anolyte 0.9 M $SO_2$ in 3 M $H_2SO_4$, 3.7 cm $min^{-1}$; catholyte: 3 M $H_2SO_4$ static; membrane: RAI-4010; 25 °C. $R_{int} = 0.1\ \Omega$. Polarization curves are corrected for internal resistance losses.

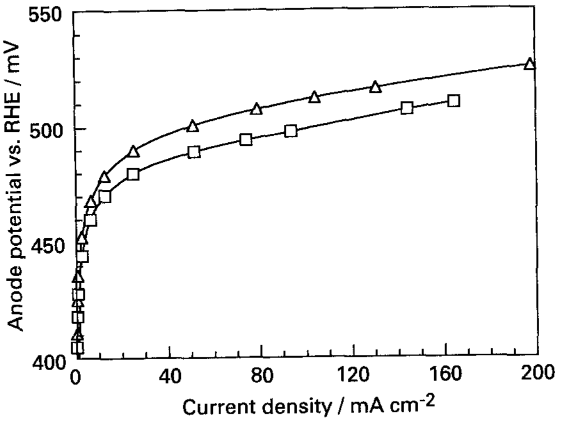

Fig. 3. Anode polarization curves. (□) Pt–Al electrode (1 mg Pt $cm^{-2}$, 10 at % Al), (△) Pt electrode (1 mg Pt $cm^{-2}$, no Al). (Same conditions as Fig. 2.)

However, it is currently uncertain whether or not true alloy formation between platinum and aluminium occurs and what size or arrangement of clusters would best promote $SO_2$ oxidation. The catalyst particle sizes in this bimetallic electrocatalyst were too small for resolution by X-ray diffraction, so that the presence or absence of alloying could not be determined. Also, highly dispersed electrocatalyst crystallites on large surface area support might well have compositions different from bulk metal compositions. Therefore, in this work, the electrocatalytic reaction itself serves as the probe to obtain evidence of synergistic interaction between platinum and aluminium.

Since a very small amount (1 at %) of aluminium could increase the platinum activity as much as 35%, some metal–metal electronic interaction could be anticipated. Therefore, the electronic state of highly dispersed platinum electrocatalyst was studied

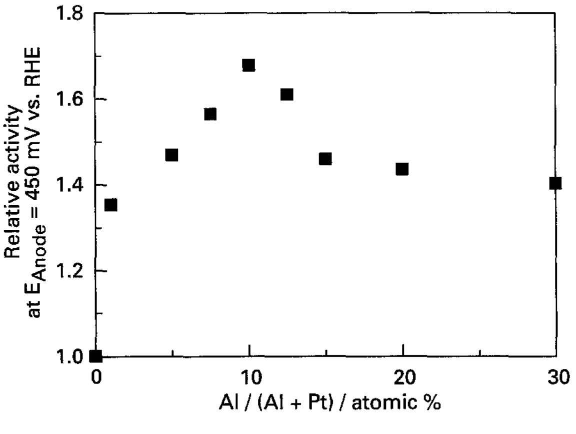

Fig. 4. Relative electrocatalytic activity of platinum–aluminium bimetallic electrocatalysts for $SO_2$ oxidation.

further with a Perkin–Elmer PHI 5400 ESCA system. Vulcan XC-72R-supported platinum and platinum–aluminium (Al/(Al + Pt) ratio: 10 at %) electrocatalysts were investigated at the same platinum loading (10 wt % platinum based on the Vulcan XC-72R weight). The electrocatalyst powder was attached to the adhesive copper tape and loaded in the instrument. There was a 0.20 eV shift in Pt $4f_{7/2}$ binding energy between the platinum and the platinum–aluminium electrocatalysts. This result appears to confirm that there is an electronic interaction between platinum and aluminum, and that part of the aluminium in the electrocatalyst might be present in the form of a platinum–aluminium alloy. This type of electronic interaction may be responsible for the change in platinum electrocatalytic activity for $SO_2$ oxidation through a modification of adsorption strength of substrates through alloy formation [28].

### 3.3. *Effect of heat treatment on platinum surface area*

To attempt to determine a proper sintering procedure for small platinum and aluminum crystallites by heat treatment, the platinum surface areas of catalysts before and after heat treatment were investigated using an electrochemical hydrogen adsorption technique to measure platinum surface area [29, 30]. In an electrochemical three-compartment cell [31], samples were loaded on graphite cloth (Electrosynthesis, GC-14) with 5 wt % Teflon binder (Du Pont, Teflon 30B).

Unfortunately, platinum surface area measurement for the platinum–aluminium electrocatalyst was not amenable to this approach. We observed what appeared to be hydrogen spillover phenomena from platinum to aluminium. The measured platinum surface for the platinum–aluminium electrocatalyst area seemed to be considerably higher than that for pure platinum electrocatalyst. It was noted, in a study of platinum intermetallic compounds, that ligand bonding between platinum and the other metal could alter the heat of adsorption of strongly bonded species such as hydrogen and carbon monoxide relative to that for pure platinum [32]. The electronic interaction between platinum and aluminium appears to change the hydrogen adsorption characteristics of platinum. Therefore, the electrochemical measurement of surface area was done only on the pure platinum electrocatalyst to gauge a reasonable heat treatment temperature for particle agglomeration.

The platinum surface area of the original Vulcan XC-72R-supported platinum electrocatalyst was $159\,m^2\,(g\,Pt)^{-1}$; after heat treatment at 930 °C for 1 h under argon, it was $64\,m^2\,(g\,Pt)^{-2}$. The calculated area was based on $210\,\mu C\,cm^{-2}$ platinum from the hydrogen desorption area [29, 30]. This platinum surface area reduction was 60%, equivalent to a particle size change from 1.5 to 3.7 nm, based on the empirical formula, $D = 1/d$, where $D$ is a dispersion expressed as a ratio and $d$ is a particle size (nm) [32]. Assuming spherical platinum particles, this particle size increase represents an agglomeration of about 20 small platinum particles into one large particle.

## 4. Conclusion

Incorporation of aluminum in carbon black-supported platinum electrocatalysts significantly increased overall electrocatalytic activity for $SO_2$ oxidation. The synergistic effect of aluminium was observed when amounts of aluminium, as small as 1 at % were incorporated with the platinum. A maximum of 68% increase in electrocatalytic activity improvement was observed for 10 at % aluminium incorporated in highly dispersed platinum crystallites. Electronic interaction between platinum and aluminium was indicated both by an ESCA study of particles and electrochemical platinum surface area measurements.

Although the main objective of this study was to investigate effects of aluminium on platinum, further investigation of efficient mixed electrocatalyst preparation methods with minimization of surface area reduction will lead to further enhancement of electrocatalytic activity.

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