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Catalytic and Electrocatalytic Oxidation of Acetate

Electrocatalysis refers to electrode processes, the rates of which are dependent on the nature of the electrode. It is a form of heterogeneous catalysis where an overall charge transfer across the electrode–solution interface takes place. A chemical reaction in solution, which is catalyzed by a conducting surface, is likely to involve charge transfer with the catalyst, i.e., it will take place by anodic and cathodic electrochemical processes. In this case, catalysis and electrocatalysis will be closely related since the catalytic activity of a material for such a reaction will be a combination of its electrocatalytic activities for the individual processes.

The concept of simultaneous anodic and cathodic processes is well established in the fields of corrosion and displacement reactions (*1, 2*). In the field of heterogeneous catalysis it has been applied to a few systems (*3–7*). In this communication, it is shown that the platinum catalyzed reaction between acetate and oxygen,

$$CH_3COO^- + H^+ + 2O_2 \rightarrow 2CO_2 + 2H_2O, \quad (1)$$

takes place through the electrochemical processes,

$$CH_3COO^- + 2H_2O \rightarrow 2CO_2 + 7H^+ + 8e, \quad (2)$$

and

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O. \quad (3)$$

The electro-oxidation of acetate to carbon dioxide, reaction (2), has been shown (*8*) to proceed on platinum at potentials lower than 0.7 V against a reversible hydrogen electrode and its rate is determined by the first electron transfer. The electroreduction of oxygen, reaction (3), is well documented (*9, 10*).

Electrochemical mechanisms of this type must be expected for other heterogeneously catalyzed organic oxidations in solution as well as the more obvious charge transfer reactions such as the iron(III)–iodine reaction discussed by Spiro (*7*).

The rate of an electrode process is dependent on the potential across the electrode–solution interface. When a catalytic process takes place by individual electrode processes, a steady state potential is set up which must be such that the rates of the anodic and cathodic processes are equal and opposite since there is a zero net current. If the processes occur at the same rates in the presence and absence of each other, then the catalytic activity can be predicted exactly from the electrochemical properties of the individual proc-

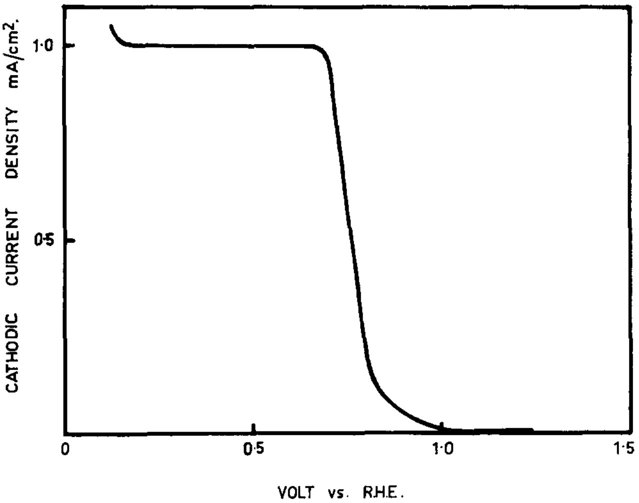

FIG. 1. Steady state current–potential curves for oxygen reduction in oxygen saturated solution of 0.9 *M* CH_3COONa, 0.1 *M* CH_3COOH on smooth platinum at 25°C.

esses. However, if there are two opposing reactions which both proceed through adsorbed intermediates, there will be interference between these reactions unless the steady state coverage of intermediates is very small. If the complete mechanism is known it may be possible to determine to what extent each process will affect the rate of the other process. The situation is simplified, if one reaction is controlled by mass transport. In this case one reactant concentration at the catalyst surface, and therefore the coverage of intermediates in its reaction, will approach zero and there will be negligible interference with the other process. This is found to be the case for reaction (1) when its rate is controlled by mass transport of oxygen.

EXPERIMENTAL METHODS

For the study of the platinum catalyzed acetate–oxygen reaction, a three-compartment glass cell of conventional design for electrochemical studies was used. The compartments containing the working and platinum counter electrodes were thermostated at temperatures in the range 25–94°C, while that containing a mercury–mercurous sulfate reference electrode was maintained at room temperature. All potentials reported have been converted to the scale of the reversible hydrogen electrode in the solution under study. The potential was controlled with a 68TS1 Wenking potentiostat. A solution containing 0.9 *M* sodium acetate and 0.1 *M* acetic acid was used for all experiments.

Three electrodes were used with roughness factors (RF), i.e., the ratio of real to geometric surface area, of 8.3, 112, and 1500; the former two were platinized platinum while the latter was of precipitated platinum black, bonded in Teflon.* Platinized platinum electrodes were prepared by electrodeposition at 25°C from a 2% chloroplatinic acid solution in 1 *M* hydrochloric acid at a controlled potential of +0.05 V. The real surface area of the electrodes was determined from the hydrogen adsorbed during a linear potential sweep, assuming the saturation hydrogen coverage to be equivalent to 210 $\mu C/cm^2$ (*11*). The electrodes were activated by pulsing the potential between 0.4 and 1.5 V.

Electrochemical measurements were made with a stationary electrode in stirred solution. The oxygen current, being controlled by mass transport, was dependent on the stirring rate and projected electrode surface area. On the other hand the acetate current, being activation controlled under the experimental conditions, was inde-

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* Cyanamid fuel cell electrode type AA-1.

pendent of stirring rate and proportional to the real area of the electrode (*12*). The stirring rate was adjusted to maintain the limiting oxygen reduction current in the region of 1 mA/geom cm^2. The electrode roughness changed by a factor of 180 and therefore, at constant temperature and potential, the acetate currents with the three electrodes differ considerably while the oxygen currents are similar.

Individual Current–Potential Curves

The reduction of oxygen at a smooth platinum electrode at 25°C, i.e., conditions where acetate electro-oxidation is negligible, is shown in Fig. 1. As shown the cathodic current increases with decrease in potential to reach a limiting value at ~0.65 V. Current–potential curves for acetate electro-oxidation were determined in solution deoxygenated with nitrogen which was purified by passage over a column of copper deposited on kieselguhr (*13*) and through a liquid air trap. Curves for the electrode of RF 1500 at temperatures of 40–94°C are shown in Fig. 2; here the current is plotted on a logarithmic scale to include data over a large range of values. The limiting oxygen reduction current must be determined under the same conditions of stirring rate, temperature, and solution composition as for the overall catalytic process since it will vary with all these factors. This was achieved by bubbling oxygen through the cell after each acetate curve was recorded and measuring the oxygen current at potentials where both acetate oxidation and hydrogen evolution are negligible, i.e., 0.1–0.15 V. Small changes in potential did not change the value of the current, confirming that it is a limiting current and it can, therefore, be assumed to be constant up to 0.65 V. The circuit was then opened and the potential was measured. The equilibrium potential was independent of the potential of the electrode before the circuit was opened. A comparison of the experimental open circuit potentials with those calculated from where the oxygen and acetate currents are equal and opposite are shown in Table 1; except for the situation where the potential is >0.7 V, discussed below, the potentials (observed and calculated) are equal within the experimental error.

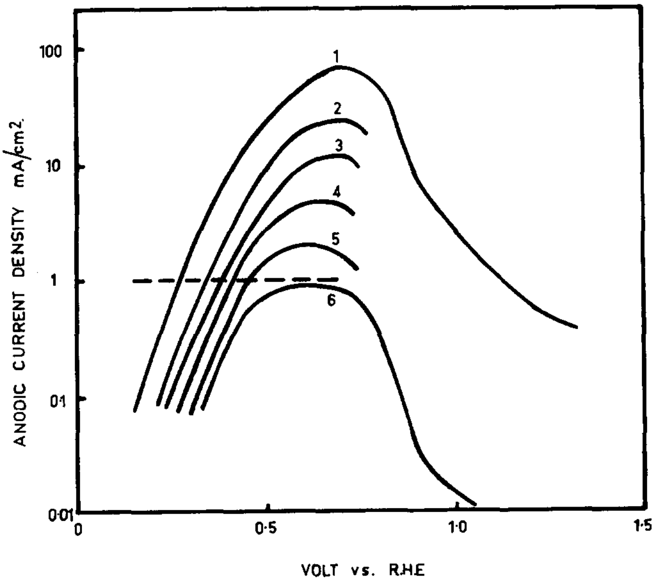

FIG. 2. Steady state current–potential curves for acetate oxidation in deoxygenated solution of 0.9 *M* CH_3COONa, 0.1 *M* CH_3COOH: platinum electrode of RF 1500 at temperatures of (1), 94; (2), 80; (3), 70; (4), 60; (5), 50; and (6) 40°C; (- - -), the acetate current necessary to equal the oxygen current. Therefore the open circuit potential in oxygen saturated solution will be where this line crosses curves 1–6.

TABLE 1

COMPARISON OF EXPERIMENTAL OPEN CIRCUIT POTENTIALS IN OXYGEN SATURATED ACETATE SOLUTION WITH THOSE CALCULATED FROM THE INDIVIDUAL CATHODIC AND ANODIC PROCESSES

Temp. (°C)	Limiting oxygen current (mA/cm²)	Maximum acetate current (0.65 V) (mA/cm²)	Open circuit potential V vs. RHE	
			Exp.	Calc
(i) RF 1500				
94	1.0	65	0.28	0.27
80	1.0	26	0.33	0.34
70	1.1	11	0.38	0.38
60	1.0	5.2	0.40	0.41
50	1.1	2.0	0.45	0.45
40	1.0	0.90	1.05	>0.7
(ii) RF 112				
94	0.80	10	0.38	0.38
80	0.80	4.1	0.43	0.43
70	0.75	1.2	0.51	0.50
60	0.80	0.60	1.05	>0.7
(iii) RF 8.3				
94	0.30	0.39	0.49	0.50
94	0.75	0.39	1.05	>0.7

Product Analysis

The assumption that, on open circuit, carbon dioxide is produced at a rate equal to the oxygen reduction current was confirmed by determining the quantity of carbon dioxide produced at a 20-cm^2 electrode of RF 1500 in oxygenated acetate solution at 80°C. It was determined gravimetrically by absorption in soda lime; the value of 0.26 mg/min is in good agreement with that of 0.28 mg/min calculated from the oxygen reduction current.

DISCUSSION

The rate of the catalytic process is controlled by the rate of oxygen reduction. Therefore as the electrocatalytic activity for acetate oxidation is decreased, by a decrease in temperature or surface roughness, the open circuit potential becomes more positive. As shown in Figs. 1 and 2, both acetate oxidation and oxygen reduction are inhibited at potentials >0.7 V; this is due to adsorption of oxygen on the platinum electrode. The adsorption of oxygen on platinum occurs at potentials >0.7 V in all aqueous solutions; the oxygen is obtained by a charge transfer process from water and so the presence of dissolved oxygen is not required. If the oxygen cathodic current at potentials <0.7 V is greater than the maximum acetate anodic current, the equilibrium open circuit potential can never be in the region where the electrode is active to both acetate oxidation and oxygen reduction since there is no potential in this region, where the two currents are equal and opposite (Fig. 2, curve 6). Under these circumstances, the potential will be in a region where the oxygen current has less than its limiting value and therefore the steady state potential cannot be obtained accurately from studies of the individual processes since the oxygen current at this potential cannot be determined under the same conditions of solution composition and temperature. However the potential must be >0.7 V. Therefore, at constant oxygen current, there is a critical temperature or roughness factor where the electrode potential and the catalytic activity for the acetate–oxygen reaction change abruptly from a region of activity (<0.7 V) to one of inhibition (>0.7 V); this change is reversed by restoring the conditions corresponding to the active state. The actual change from 0.5 to 1.05 V (Table 1) represents a difference in acetate current, and therefore catalytic activity, of about two orders of magnitude (Fig. 2).

Furthermore a situation can be reached, as shown in Table 1 for the lowest roughness electrode, where an increase in the rate of transport of oxygen to the electrode, resulting from an increase in stirring rate, can cause a sudden decrease in catalytic activity to a very small value, as the catalyst adsorbs oxygen and its potential moves into the passive region. That is, the rate of the catalyzed reaction increases linearly with increase in the rate of transport of oxygen up to a critical transport rate above which the reaction rate drops by about two orders of magnitude. This behavior can only be understood from electrochemical investigations of the current–potential behavior of the two electrode processes which constitute the overall catalysis.

It was shown that the characteristics of platinum catalyzed acetate–oxygen reaction can be predicted from the electrochemical studies of the individual processes. The electrochemical approach is, therefore, a valuable method for studying catalytic processes in solution.

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