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The role of low coverage sodium surface species on electrochemical promotion in a Pt/YSZ system

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Abstract:

The effect of sodium-modification on the catalyst and electrocatalytic properties of a platinum catalyst supported on a YSZ solid electrolyte was studied. Increasing the sodium coverage on the catalyst surface appears to block some of the three-phase boundary (*tpb*) sites and reduces the rate of the charge transfer reaction. The promotion of the platinum surface reaction (ethylene oxidation) seems to a first approximation to be a function of the rate of oxygen supply or removal to or from the surface irrespective of whether this is contaminated by sodium or not (samples with sodium contamination require a higher overpotential to achieve the same current density as a clean sample because of poisoning in the *tpb*). At high negative polarisations (oxygen removed from the surface) the sodium contaminated samples show a significant increase in rate, possibly due to the decomposition of e.g. sodium hydroxides and carbonates.

Keywords:

EPOC, Pt, YSZ, Na species, Cyclic voltammetry, Oxygen charge transfer, Ethylene oxidation

1. Introduction

Electrochemical Promotion of Catalysis (EPOC) has been observed in a wide range of reactions performed on various metal catalysts supported on a number of different solid electrolytes [1-4]. In EPOC, or NEMCA (non-faradaic electrochemical promotion of catalysis), a small current supplied through an external circuit results in promoting species being pumped towards the catalyst surface, thus modifying the catalytic activity and selectivity of a reaction [5-6]. A recent study found that variations in the catalyst surface morphology and the presence of impurities on the catalysts may have a significant impact on the catalyst behaviour [7] and could play an important role in electrochemical promotion. Nevertheless, the role of impurities in EPOC has not been studied in detail except perhaps the influence of Si impurities and electrode morphology on the Pt(O₂)/YSZ system using cyclic voltammetry [7]. In this work, in order to systematically study the role of impurities in EPOC, a known type and amount of impurity (in this case sodium, Na) is gradually deposited in increasing amounts onto a nominally 'clean' catalyst surface (in this case platinum, deposited on yttria stabilised zirconia, YSZ) and the catalyst used for EPOC studies of ethylene oxidation.

2. Experimental

The catalyst/electrode and electrolyte materials used in the study were metal resinsates provided by Metalor, UK and 8 mol% YSZ provided by Pi-Kem Ltd., UK. The platinum resinate was painted on two YSZ dense pellets of 15 mm diameter and 2 mm thickness and sintered at 850°C for 2 hrs. The resulting samples have a platinum film of geometric projected surface area, $A = 0.88 \text{ cm}^2$. One sample was used for the non-reactive study and the other was used under reactive conditions. A three electrode pellet system, with platinum as a working electrode/catalyst and gold as the counter and reference electrodes supported on a YSZ pellet, was mounted in a single chamber type electrochemical reactor (i.e. all electrodes

were exposed to the same gas atmosphere) already described elsewhere [8]. The pellet system was either exposed to 20 kPa of oxygen at 400°C (for non-reactive conditions) or a mixture of oxygen and ethylene at 350°C (for reactive conditions). All experiments were conducted at atmospheric pressure. In the latter, the oxygen partial pressure was varied between $p_{\text{O}_2} = 0.5$, 1.5, 3 and 8 kPa, while the ethylene partial pressure was kept constant at $p_{\text{C}_2\text{H}_4} = 0.5$ kPa. The gases used were 20% O₂/He and 10% C₂H₄/He provided by BOC, UK. The total gas flow in all experiments was 200 ml min⁻¹ (STP). Gas analysis was carried out by a BINOS 100 CO₂ analyser. Sodium was gradually deposited on the surface of the platinum catalyst dropwise using solutions of increasing concentrations prepared by dilution of 1 M NaOH, and dried in air at 400°C in the same reactor. In the rest of the manuscript the sodium-modified samples are referred to in terms of the sodium coverage). Table 1 shows the sodium loading of each sample used in this work. The sodium loading (atoms of sodium) per platinum surface area and the percentage of sodium coverage are also shown. For an estimation of the platinum surface area, a mean platinum particle size of 0.5 µm determined from SEM analysis (not shown here) was used; a spherical geometry was assumed. The 10 mg masses of the platinum films thus correspond to about 56 cm² of platinum surface area (note that because of the uncertainty in the platinum surface area specific rates and current densities reported later use the platinum projected area). The percentage of sodium coverage on the platinum surface is calculated assuming that full coverage (i.e. one monolayer of sodium) is achieved at sodium loading of approximately 10¹⁵ Na atoms cm⁻² based on experimental values from the literature [9-10]. Sodium modification of the kinetics of the oxygen charge transfer reaction and ethylene oxidation on the Pt/YSZ system was investigated using cyclic voltammetry following on from an early study by Vayenas [11-12], and using EPOC-type electrocatalytic experiments [1-2]. The potential range used in the cyclic voltammetry experiments was from

0.3 to -0.5 V at a scan rate, $\nu = 30 \text{ mV s}^{-1}$ for the non-reactive study, and 1.0 to -1.0 V at $\nu = 5 \text{ mV s}^{-1}$ for reactive conditions.

3. Results

3.1 Non-reactive conditions (oxygen charge transfer reaction)

Fig. 1a shows cyclic voltammograms of the platinum catalyst exposed to an oxygen flow of 20 kPa at 400°C, at a scan rate, $\nu = 20 \text{ mV s}^{-1}$. The voltammograms were obtained using one sample to which was gradually added NaOH of varying concentration from 10^{-12} to 10^{-1} M as shown in Table 1. As discussed earlier the sodium coverage in these samples ranges from $5.4 \times 10^{-9} \%$ ($[\text{NaOH}] = 10^{-12} \text{ M}$) to full coverage ($[\text{NaOH}] = 10^{-1} \text{ M}$). One of the main features on the voltammograms is the sharp cathodic peak that involves the reduction of oxygen at the metal-solid electrolyte-gas three phase boundaries, *tpb*, into oxygen anions [11]. The sharp peak may indicate that oxygen adsorption and/or oxygen surface diffusion are slower than charge transfer. The cathodic peak current, i_{pc} and the peak area, A_{pc} are shown in Fig 1b. As can be seen in this figure an increase in the sodium coverage causes a decrease in the i_{pc} , and in the peak area (i.e. the charge transferred during the oxygen reduction at the *tpb*). It is postulated that sodium-containing species may preferentially populate the *tpb* thus blocking the available sites for oxygen reduction as very low sodium coverages (between $5 \times 10^{-9} \%$ and 0.5%) would not be expected to have an effect on the bulk of the platinum surface but do cause a dramatic change in the charge transfer behaviour of the system. It is interesting to note that at full sodium coverage larger current densities and greater hysteresis in the response are observed possibly indicating that charge transfer is governed by a different mechanism. As the measurements discussed here were performed under non-reactive

conditions the role of any sodium present on the catalyst surface (if any) cannot be assessed at this stage.

3.2 Reactive conditions (ethylene oxidation)

A study of the effect of sodium addition on the Pt/YSZ system under reactive conditions was conducted using ethylene oxidation as a probe reaction. First, cyclic voltammograms of ‘clean’ and sodium-modified platinum catalyst (with 1 μL of 10^{-4} M NaOH or equivalent to 0.54% sodium coverage) were recorded at 5 mV s^{-1} under flow of 3 kPa O_2 and 0.5 kPa C_2H_4 at 350°C . The OCP of the clean system was -215 mV and that of the sodium-modified sample was -265 mV. The change in the rate of CO_2 (area specific rates calculated using $A = 0.88 \text{ cm}^2$) produced from ethylene oxidation during the cyclic voltammetry experiment is depicted in Fig. 2a as a function of the current density during polarisation. The corresponding current density versus overpotential response is shown in Fig. 2b. In Fig. 2a we can observe that the rate change in both systems follows a similar pattern, i.e. the CO_2 production rate is decreased for positive current densities and increased for negative values¹. We can see that the reaction rate of the two systems reaches approximately the same minimum at current densities of the order of $+20 \mu\text{A cm}^{-2}$ and the same maximum at a current density of about $-15 \mu\text{A cm}^{-2}$. The catalytic rate is clearly influenced by current in a similar way for the two samples. This is consistent with sodium poisoning the *tpb* while sodium-containing species do not appear to have a significant role (at least at this coverage) on the rest of the surface.

¹ In previous studies on the EPOC of ethylene oxidation over a platinum catalyst it has been found that positive polarisation generally enhances the rate of ethylene oxidation (i.e. the reaction shows electrophobic behaviour) [S. Bebelis, C.G. Vayenas, Journal of Catalysis, 118 (1989) 125, D. Poulidi, I. Metcalfe, Journal of Applied Electrochemistry, 38 (2008) 1121, M. Stoukides, C.G. Vayenas, Journal of Catalysis, 70 (1981) 137]. However, it has also been found that at temperatures higher than 350°C (as in the case studied here) negative polarisation may also cause a small rate increase [C. Koutsodontis et al, Topics in Catalysis, 38 (2006) 157]. In addition, depending on the gas phase composition (i.e. the $p_{\text{O}_2}/p_{\text{C}_2\text{H}_4}$ ratio) it is possible to observe a rate enhancement under both positive and negative polarisation [S. Bebelis et al, Solid State Ionics, 129 (2000) 33]. One possible cause for the range of behaviour observed in the different studies (including the work presented here) could be the presence of uncharacterised and unquantified impurities in the different platinum catalysts.

Next, we investigate the rate changes observed for both systems under a constant polarisation (at $\eta = +1$ V and -1 V). Fig. 3 shows a typical plot of the reaction rate (production of CO_2) transient under positive polarisation overpotential, $\eta = +1$ V (Fig. 3a), and under negative polarisation, $\eta = -1$ V (Fig. 3b) using a mixture of 1.5 kPa O_2 and 0.5 kPa C_2H_4 at 350°C . In both cases we can see that the open circuit rates of the two systems are very similar (around $65 \text{ nmol s}^{-1} \text{ cm}^{-2}$). This observation supports further our hypothesis that under these conditions the sodium-containing surface species has little influence on the catalytic activity. In Fig. 3a we observe again a decrease in the CO_2 rate upon application of a positive potential. Both the open circuit and the polarised rates of the two systems are very similar. It can be observed that the time constant associated with rate change is longer for the sodium-modified sample consistent with a slower rate of charge transfer for this sample. Negative polarisation, as can be seen in Fig. 3b, has a more pronounced effect on the sodium-modified sample. Under open circuit conditions, the CO_2 production rate of the ‘clean’ system is $63 \text{ nmol s}^{-1} \text{ cm}^{-2}$ and that of the sodium-modified system is $65 \text{ nmol s}^{-1} \text{ cm}^{-2}$, while for $\eta = -1$ V, the rate increases to $80 \text{ nmol s}^{-1} \text{ cm}^{-2}$ (‘clean’ system) and $132 \text{ nmol s}^{-1} \text{ cm}^{-2}$ (sodium-modified system)². It is clear that sodium modification affects the rate enhancement and the non-faradaicity of the observed promotion in this case. This behaviour could suggest that under negative polarisation, i.e. removal of oxygen from the catalyst surface, activation of the sodium-containing species on the catalyst surface occurs. These species may be in the form of hydroxides and carbonates at low overpotentials that would essentially be spectator species in the experiments described earlier. These species may decompose on application of a large steady negative potential as is the case here generating species that can promote surface

² The rate enhancement ratios, $\rho = r_{\text{oc}}/r_{\text{pol}}$ and the Faradaic efficiencies, $\Lambda = 2F(r_{\text{pol}}-r_{\text{oc}})/i$ (where, r_{oc} is the open circuit rate, r_{pol} the polarised rate, i is the measured current density at polarisation and F is Faraday’s constant) for the two systems are $\rho_{\text{clean}} = 1.27$ and $\Lambda_{\text{clean}} = -177$, and $\rho_{\text{Na}} = 2.03$, $\Lambda_{\text{Na}} = -871$ respectively.

reactions. This behaviour is very interesting and warrants further investigation to be fully understood.

The same experiment was also conducted using different gas compositions, where the oxygen flow was varied from 0.5 to 8 kPa and the ethylene flow kept at 0.5 kPa. In this experiment, the open circuit potential, OCP was in the range of -51 to -253 mV. Fig. 4a shows the CO₂ production steady state rate at open circuit and under polarised conditions ($\eta = \pm 1$ V), while Fig. 4b depicts the corresponding rate enhancement ratios. As we can observe and as we discussed earlier on, the difference in the open circuit rate of both systems in Fig. 4a is not very significant in all the conditions studied here. As far as the induced rate modification is concerned Fig. 4b shows that the ρ values of the sodium-modified system are almost always higher than the 'clean' system, except under oxygen-rich conditions ($p_{O_2} = 8$ kPa). In fact, the rate enhancement by sodium modification is most significant when the system is under lean conditions (ρ is highest at a mixture of 0.5/0.5 kPa oxygen/ethylene).

4. Conclusions

From our study, we have shown that addition of sodium to a platinum catalyst surface can affect, to some extent, the characteristics of the oxygen charge transfer reaction and modify the activity of a catalytic reaction. Sodium surface species (which could be in the form of e.g. hydroxides or carbonates) block sites in the *tpb* region and slow down the charge transfer reaction. They may also slightly reduce the open circuit rate of a catalytic reaction (in this case ethylene oxidation) by a surface blocking mechanism. However, on the application of large negative overpotentials these sodium-containing species may decompose leading to the formation of promoting species that cause an increase of reaction rate.

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Figure Captions / Table Captions

Table 1. Sodium loading and percent coverage of the samples

Fig. 1: Effect of sodium addition on the cyclic voltammetry under non-reactive conditions: (a) Cyclic voltammograms of ‘clean’ and sodium-modified platinum catalyst scanned at 20 mV s⁻¹ between 0.3 to -0.5 V; $p_{O_2} = 20$ kPa O₂; Temperature, $T = 400^\circ\text{C}$; Total flow rate, $f = 200$ ml min⁻¹; i_{pc} = cathodic peak height; (b) Effect of varying sodium coverage on the cathodic peak height, i_{pc} and the peak area, A_{pc} .

Fig. 2: Effect of sodium addition on the rate of CO₂ production during cyclic voltammogram of platinum catalyst exposed to a gas mixture of 3 kPa O₂ and 0.5 kPa C₂H₄ at 350°C (reactive conditions): (a) CO₂ production rate for ‘clean’ and sodium-modified platinum catalyst (with 1 µL of 10⁻⁴ M NaOH) versus current density, i ; (b) Current density, i versus U_{WR} . The voltammograms were scanned at 5 mV s⁻¹ between 1 and -1V, starting from 0 V.

Fig. 3: Effect of sodium addition on CO₂ transients of platinum catalyst (a) CO₂ rate under positive polarisation overpotential, $\eta = +1$ V; (b) CO₂ rate under negative polarisation, $\eta = -1$ V. Sodium added is 1 µL of 10⁻⁴ M NaOH; Gas composition: 1.5 kPa O₂ and 0.5 kPa C₂H₄; Temperature, $T = 350^\circ\text{C}$. Total flow rate, $f = 200$ ml min⁻¹.

Fig. 4: Comparison of CO₂ production rate during open and closed-circuit conditions for ‘clean’ and sodium-modified platinum catalyst (with 1 µL of 10⁻⁴ M NaOH); Gas composition: 0.5, 1.5, 3.0 or 8.0 kPa O₂ and 0.5 kPa C₂H₄; Temperature, $T = 350^\circ\text{C}$; Total flow rate, $f = 200$ ml min⁻¹; OC = Open circuit rate; P = Polarised rate (± 1 V).

Fig. 1a

Fig. 1b

Fig. 2

Fig. 3a

Fig. 3b

Fig. 4