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Influence of impurities and catalyst surface characteristics on the oxygen charge transfer reaction in the Pt/YSZ system

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Abstract

Spillover processes (i.e. the migration of ionic species from the support to the catalyst and vice versa) are known to play a very important role in catalysis and electrocatalysis. These spillover processes can be influenced by impurities (pre-existing on the catalyst surface) and the catalyst morphology that may differ as a result of the differences in catalyst manufacturing processes. This work investigates the influence of impurities present in three commercial platinum (Pt) resins. The resulting Pt films studied here were supported on yttria-stabilised-zirconia (YSZ). It was found that the three different catalyst films contained a range of impurities (determined by ICP-OES) that appear to affect the oxygen charge transfer reaction as studied by cyclic voltammetry (CV). This has implications for the design of electrocatalytic experiments.

Keywords: Solid state cyclic voltammetry, Electrochemical promotion, Pt film impurities

Introduction

Electrochemical promotion of catalysis (EPOC) or non-Faradaic electrochemical modification of catalytic activity (NEMCA) has been studied and applied successfully for many catalytic systems [1-5]. In EPOC, catalytic activity and selectivity of metal films in

contact with electrolytes, both solid state and aqueous, can be varied *in situ* in a very pronounced and reversible manner via electrical potential application between the catalyst film and a counter electrode also in contact with the electrolyte [1]. EPOC is shown to be due to the catalytically promoting properties of ionic spillover species that migrate onto the catalyst surface under the influence of the applied potential. These species accompanied by their compensating charge in the metal establish an overall neutral double layer on the gas exposed catalyst surface. The effective double layer affects the binding strength of chemisorbed reactants and reaction intermediates and thus affects the catalytic rate [6].

Catalyst films are often prepared by using different methods and materials. The resulting catalyst films, therefore, may have different microstructure or morphology [7, 8] and impurities [8, 9]. Pt/YSZ systems with catalyst films of different microstructures or morphology may result in significant differences in the three phase boundary (*tpb*) length (i.e. the solid electrolyte – catalyst – gas interface where the electrochemical reactions take place). This can affect the electrochemical behaviour of the system. In addition, the different impurities may affect both the catalytic and electrochemical properties of the system. Depending on the nature of the impurities they may hinder (by blocking the catalyst active sites or the *tpb*) or enhance (if catalytically active) the catalytic or electrocatalytic activity. To date, very little information is available on the possible influence of impurities on EPOC. Table 1 shows the impurities found in platinum and YSZ prepared by different methods as published in previous studies. In Pt and YSZ samples, silicon (Si) has been known as the main contaminant. Even high purity electrolyte and electrode materials are often Si-contaminated as observed in the work of Mutoro et al [8]. The main aim of the present study is to investigate the influence of impurities and catalyst surface characteristics of three different Pt catalysts films supported on YSZ on the oxygen charge transfer reaction.

Experimental

In this work, porous electrodes were prepared by using commercial Pt paste and resins from three different providers that were ESL (5542), Heraeus (RP 10003-12) and Metalor (98007). The oxygen charge transfer reaction for Pt/YSZ systems using the three different commercial catalysts were studied by cyclic voltammetry (CV) and compared. The electrolyte pellets were prepared by pressing approximately 2.2g of YSZ powder (8 mol% yttria) at 3 tons by using a 20mm diameter die. The YSZ pellets were sintered at 1500°C for 4 hours. The sintered YSZ pellets were polished with SiC paper and washed with isopropyl alcohol in an ultrasonic cleaner and then rinsed with deionised (DI) water and dried. The electrochemical cell used in the current work was of the single chamber type and consisted of a three electrode system (working, reference and counter electrodes) [10]. The working electrode used in the current work was platinum (Pt) catalyst that was deposited on the prepared YSZ pellets on one side of the pellet by using a brush and then sintered by using a specific sintering program. The ESL catalyst was sintered at 980°C for 10 and 60 minutes, the Metalor catalyst at 800°C for 2 hours and the Heraeus catalyst at 850°C for 5 minutes. The two different sintering times for the ESL catalyst were used in order to investigate the effect of sintering time on impurity levels (e.g. impurities could be volatilised during sintering) and variations in catalyst morphology. In all cases the geometric projected surface area of the Pt electrodes was approximately 0.88 cm². This surface area has been used in the current density calculations presented later on. The effect of temperature treatment time on impurities (metal) concentration removal has been described by Winkel et al [11]. Gold (Au) was used as the reference and counter electrodes and was deposited on YSZ pellets by using a brush and sintered at 400°C and 800°C for 2 hours.

The three commercial resins and the sintered catalyst films were tested for metal impurities by using inductively coupled plasma optical emission spectrometry (ICP-OES). The elements

that were investigated were Pt, Bi, Si, K, La, Ag, Pd, Rh, Mn, Au, Al, Cu, Pb, Zn, Na, Fe, Ni, Cr, Ca and Mg. K, La, Ag, Pd, Rh, Mn, Pb and Cu were either not present or below the detection limit of the equipment. The investigated elements for the catalysts film were Pt, Bi, Si, Ag, Au, Al, Pb, Zn, Na, Ni, Cr, Fe, Ca and Mg. For the ICP analysis a blank (aqua regia) and a deionised water sample were also analysed in order to deduct impurities found in the aqua regia and deionised water used to prepare the samples.

The catalyst surface characteristics (such as porosity and grain size) and also distribution of different elements (chemical composition) were investigated via scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX), respectively. The oxygen transfer reaction on the Pt/YSZ system was investigated by cyclic voltammetry experiments using an IVIUM Compactstat unit. The experiments were carried out under nonreactive conditions. In the experiment, a flow of 200 mL/min 20% O₂/He was passed through the electrochemical reactor. The experiments were conducted for six different scan rates ($v = 1, 5, 20, 30, 50$ and 100 mV/s) and for each v the experiment was repeated for three cycles. The applied potential between the reference electrode and the working electrode and reactor temperature was 0.5 V to -1.0 V and 400°C, respectively.

Results and Discussion

Catalyst Characterisation

Fig. 3.1 shows SEM images of the Pt films on the prepared YSZ pellets. Based on this figure, the average diameter of crystallites constituting the Pt catalyst films used in this work on YSZ ranged from 0.5 to 2 μm . SEM images indicated that ESL and Heraeus have a more porous structure compared with Metalor sample. In all cases the obtained EDX spectra did not show any peaks for elements other than Pt. This observation indicates that if there are any impurities present on the catalyst films they were below the EDX detection limit.

Next, the three Pt resins and the sintering films were analysed by ICP. The main impurities found in the three resins and the sintered catalyst films, are shown in Table 1 and Table 2. The quantitative analysis was at this point inconclusive as the level of trace elements found in the deionised water was of the same order of magnitude as the impurities in the catalysts and therefore significant error is associated with the calculation of the absolute values of the impurities concentration. As can be seen in Table 2 a range of impurities was found in all three Pt resins in concentrations that ranged from 0.001% to 1.234%wt. However, different impurities were found in the sintered catalyst films in concentration that ranged from 0.002% to 1.595%wt. This is anticipated as a lot of the impurities may migrate from the bulk to the surface of the catalyst film and volatilise during the sintering process. Moreover, some different impurities could have been introduced from the YSZ substrate during the electrode preparation. It is obvious that in terms of their effect on catalytic and electrocatalytic performance the most important impurities are those found on the catalyst films after sintering.

The sintered ESL catalyst film contained mainly Bi and Si. An interesting observation is that a lower concentration of Bi was found in the ESL catalyst film with a longer sintering time (0.185 % wt. compared to 1.595 % wt. on the 10min sample). It appears that Bi volatilises with sintering. Winkel et al[11] had shown that heavy metal concentration decrease as the temperature treatment time increases. The sintered Heraeus film contained Bi (approximately 0.336 % wt.), Pb, Ca and Si. The Metalor catalyst film showed only Bi (0.04 % wt.) as the main impurity (but in lower levels than the ESL). The ICP results indicate that the longer the sintering time of the Pt (even for catalysts from different providers) the less amount of impurities remains on the Pt surface; the Metalor film, that was sintered for 2 hours, appears to have a lower level of impurities while the Heraeus and ESL 10 min films have higher levels and more impurities remaining on the Pt surface. The different types and amounts of

impurities in each Pt/catalyst and sintered sample are expected to affect the catalytic and electrochemical properties of these catalyst/electrodes in an as yet unstudied way (as some of these elements may have promoting properties while others may cause active-site and /or *tpb* blocking).

Cyclic Voltammetry

Fig. 2 shows the voltammograms obtained at 400°C for the four catalyst films tested using a scan rate of 30 mV/s. In all case a cathodic peak is observed in the figure that corresponds to the reduction of oxygen chemisorbed at the *tpb* as described in equation (1) [12].

Anodic peaks that correspond to the reverse of the charge transfer reaction [12] are barely detectable in all of the voltammograms which indicates that $\text{O}_{(tpb)}$ was formed primarily from $\text{O}_{2(g)}$ and not from O^{2-} .

Electrode surface characteristics and impurities in the commercial Pt catalysts influence the oxidation and reduction of oxygen species in the Pt/YSZ system as is depicted in the resulted voltammograms of the ESL, Heraeus and Metalor catalysts. These are manifested in the form of differences in the current range and the shape, size and position of the cathodic peaks in the voltammograms. The current range of the four catalysts varies by almost two orders of magnitude with Heraeus exhibiting the lowest and ESL the highest currents. The current ranges of ESL 60min and Metalor were comparable.

These differences are further highlighted in Fig. 3 (where the voltammograms of the four films at varying scan rates are shown). The cathodic peaks and currents of the Heraeus voltammograms are much smaller compared to the cathodic peaks and current in the ESL and Metalor voltammograms. This could be due to the presence of Bi, Pb, Ca and Si on the Heraeus catalyst surface that suppressed the oxygen charge transfer reaction. The observed

peaks on both ESL samples are broader when compared to the Metalor and Heraeus samples. A study conducted by Arul Raj and Vasu[13] indicated that the cathodic peak broadens for an electrochemical system that contains Bi. This is in agreement with the observations of this study. In contrast, the Metalor sample has more distinct peaks compared to the other catalysts which could be due to the lowest level and type of impurities found on this catalyst surface. The findings show that impurities could have played a more important role in affecting the charge transfer reaction since a more porous structure does not necessarily produce more distinct peaks in a voltammogram.

Conclusions

The present work has shown that commercial catalysts (i) contain different types and amount of impurities and (ii) have different surface characteristic (chemical and physical) and that both of these factors affect the oxygen charge transfer reaction. The results indicate that both the catalyst microstructure and impurities have to be considered in the investigation of the spillover processes.

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Figure captions

Fig. 1 SEM images of Pt films on YSZ for Ptpaste/resins from (a) ESL 60 min, (b) ESL 10 min, (c) Heraeus and (d) Metalor at 1000 and 10000magnifications.

Fig. 2 Voltammogram of ESL 10 min, ESL 60 min, Heraeus and Metalor for scan rate of 30mV/s, reactor temperature of 400 °C and 200ml/min 20% O₂/He.

Fig. 3 Voltammogram of (a) ESL 10 min, (b) ESL 60 min, (c) Metalor and (d) Heraeus at different scan rates, v , reactor temperature 400°C, 200 ml/min of 20% O₂/He

Table captions

Table 1: Known impurities in YSZ and platinum found in the literature

Table 2: Impurities in the three commercial platinum catalysts used in this work

Response: Figures 1 c has been exchanged with Figure 1d as seen below.

Fig. 1

Table 1

System	Analytical Methods	Impurities	Ref.
YSZ (111) single crystal without Pt electrode	Tof-SIMS	Na, K, Ca, Cr, Al, C, Si, Mg, Fe	[8]
Commercial Pt paste without sintering aid	GDMS glow discharge mass spectrometry	Fe, Pd, Rh, Al, Cr, Si	[8]
Highly pure Pt	ICP-AES	Mg, Mn, Cu, Ag, Fe, Zn, Au, Ir, Ni, Pb, Rh, Al, Pd	[14]
10 mg samples of pure platinum metal	Ion Exchange Chromatography and Ge (Li spectrometry)	Au, Cu, Ir, K, La, Mn, Pd and Zn	[15]
Platinum resins/pastes	ICP-OES	Bi, Ca, Au, Zn, Fe, Ni, Cr	Present Work
Sintered Platinum films	ICP-OES	Bi, Si, Ca, Pb	Present Work

Providers	Impurities in catalysts		Impurities in sintered catalyst films	
	Impurities	Content (weight %)	Impurities	Content (weight %)
ESL	Bi Ca Au Cr Zn Fe Ni	0.12 0.17 0.02 0.02 0.02 0.01 0.01	60 min sample: Bi 10 min sample: Bi Si	0.19 1.59 0.63
Heraeus	Zn Si Fe Ni Cr Au	0.12 0.06 0.02 0.01 0.003 0.001	Bi Pb Si	0.34 0.22 0.98
Metalor	Fe Si Cr Ni Zn Au	0.04 0.03 0.01 0.004 0.003 0.001	Bi	0.04