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SURFACE ALKALI PROMOTION OF CARBON DIOXIDE HYDROGENATION FOR CONSERVATION OF CARBON SOURCES: CYCLIC VOLTAMMETRY STUDY

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Abstract

Conversion of CO_2 captured from biogas upgrading process into useful chemicals or fuels e.g. methane is an attractive route towards conservation of carbon sources. Sustainable hydrogenation route could be achieved by combining the process with hydrogen generated from water electrolysis. In this work, cyclic voltammetry was used as preliminary technique to probe the electrochemical behaviour of Na-modified Pt/YSZ as model catalyst under CO_2 hydrogenation. The reaction is irreversible and the voltammogram features are not easily distinguishable under reaction conditions. The increase in cathodic peak height and the decrease in peak potential with addition of sodium at low coverage (0.32%) indicated that the charge transfer reaction was enhanced and thus the methanation reaction could be electrochemically promoted given sufficient amount of H_2 flow. However, increasing Na coverage was found to decrease the current hysteresis possibly due to formation of sodium compounds such as carbonates or oxides that populate the three-phase-boundary (tpb) active sites, thus deactivating the catalyst.

Keywords: CO_2 utilisation; CO_2 hydrogenation; Electrochemical promotion; Sodium promoter; Cyclic voltammetry

Introduction

Biogas production from biomass and landfilling mainly composed of carbon dioxide (CO_2) and methane (CH_4) [1], if not decreased or used, could become increasingly important contributor towards the global increase in climate change. CO_2 can be converted into CH_4, which is an energy vector through several ways such as catalytic methanation reactions, biomethanation, etc. [2]. Electrochemically assisted catalytic hydrogenation of CO_2 is one of the means to produce CH_4 from CO_2. This method, known as electrochemical promotion of catalysis (EPOC) refers to a phenomenon whereby small current or overpotential application on a catalytic system results in significant changes of the catalytic activity of the reactions which exceed Faraday's Law expectation [3, 4]. The phenomenon is due to the migration (backspillover) of ionic promoting species generated at the gas-catalyst-solid electrolyte three phase boundaries (tpb), from the solid electrolyte to the catalyst surface [3].

An introduction of externally applied promoter species e.g. sodium to the catalyst surface may result in further enhancement of the electrochemical promotion of carbon dioxide

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hydrogenation in terms of higher catalytic activity and better selectivity to methane possibly due to synergistic effect between the two promoter species [5, 6]. In order to investigate the influence of alkali promoter species on electrochemical promotion of CO_2 methanation over a metal catalyst, a preliminary work investigating the electrochemical properties of a model catalyst system Pt/YSZ is conducted using cyclic voltammetry technique under flow of CO_2.

A CO_2 molecule naturally has a linear configuration, containing carbon with two oxygen double bonds that are equal in magnitude, but in opposite directions. It is known that CO_2 molecule configuration tends to change from linear to non-linear form at elevated temperature, becoming a good donor and poor electron acceptor. The carbon is electron deficient, making it an electrophile, while the oxygen atoms are nucleophiles with electrons to be shared. Together, CO_2 will be considered electrophile since the electronegativity of oxygen gives the carbon a partial positive charge [7]. Since CO_2 molecule has the tendency to accept electrons, the interfacial oxygen vacancy could abstract the atomic oxygen of CO_2 and result in the activation of CO_2 by electron attachment or dissociation as shown in Equations 1 and 2 below respectively [8]:

$$CO_2 + e^- \rightarrow CO + O^- \quad (1)$$

$$CO_2 + e^- \rightarrow CO + O + e^- \quad (2)$$

The oxygen ion released from reduction of CO_2 may then propagate to the catalyst-gas-solid electrolyte three phase boundary (tpb) where Pt catalysed the charge transfer reaction in similar way the oxygen charge transfer reaction happens in a $Pt(O_2)$/YSZ catalyst system, and contribute to the formation of cathodic peak in the voltammogram [9]:

$$O\ (tpb) + 2e^- \rightarrow O^{2-}\ (\text{cathodic sweep}) \quad (3)$$

$$O^{2-} \rightarrow O\ (tpb) + 2e^-\ (\text{anodic sweep}) \quad (4)$$

It was reported that the presence of cathodic peak(s) in a cyclic voltammogram may also be due to decomposition of oxides of Pt or impurities at the Pt/YSZ interface depending on the type and preparation of the electrodes [10]. In view of this consideration, instead of being directly dissociated to CO and O^- (or O + e^-) via Equations 4.1 or 4.2, the CO_2 molecule is expected to bond with Pt catalyst, resulting in the formation of Pt-CO_2 complex. Pt-CO_2 complex was reported to exist and formed from desorption of CO_2 molecules from the surface of Pt where the CO_2 is in CO + O reaction [11]. Previous work done on Pt/YSZ system, mostly on oxygen reduction (oxygen charge transfer) indicated the formation of similar Pt-adsorbed reactant complexes (Pt-O complex) as shown below [12]:

$$Pt + \tfrac{1}{2} O_2 \rightarrow Pt\text{-}O \quad (5)$$

The different stages of the electrochemical reduction of CO_2 on catalyst supported on a solid electrolyte such as yttria stabilised zirconia (YSZ) can be shown in Equations 6 to 10 [13]:

Adsorption and desorption of CO_2:

$$CO_2 + (s) \rightleftharpoons CO_2\ (s) \quad (6)$$

Adsorption and desorption of CO:

$$CO + (s) \rightleftharpoons CO\ (s) \quad (7)$$

Charge transfer steps:

$$CO_2 + e^-\ (s) + (YSZ) \rightleftharpoons CO\ (s) + O^-\ (YSZ) \quad (8)$$

$$O^-\ (YSZ) + e^-\ (s) \rightleftharpoons O^{2-}\ (YSZ) + (s) \quad (9)$$

Incorporation of O^{2-} ion into bulk YSZ:

$$O^{2-}\ (YSZ) + V\ddot{o} \rightleftharpoons O_O^X\ (YSZ) + (YSZ) \quad (10)$$

A two-step electron transfer model for CO_2 electrochemical reaction below shows oxygen hopping through the vacancy in YSZ [14]:

$$CO_2 + V\ddot{o} + 2e^- = O_O^X + CO \quad (11)$$

$$O_2\ (g) + 2V\ddot{o} + 4e^- \rightarrow 2O_O^X \quad (12)$$

Experimental

Solid electrolyte pellet was prepared using approximately 2.2 g 8 mol% yttria-stabilised-zirconia (YSZ) powder (Pi-Kem Ltd., UK), pressed using uniaxial hydraulic pressing and sintered at 1500°C for 4 hours in static air. The resulting pellet has approximately 15 mm diameter and 1.5 mm thickness. The Pt catalyst film acting as working electrode and Au serving as both counter and reference electrodes of the three-electrode system to be used in the electrochemical cell were deposited using Pt paste (Heraeus, UK) and Au paste (Heraeus, US) respectively on the YSZ pellet following the procedures previously published [15, 16]. A quartz single chamber electrochemical reactor of 22 mm internal diameter, 165mm length and 60cm^3 volume was placed in the middle of a tubular furnace (Vecstar, UK).

Cyclic voltammetry (CV) measurements were carried out using an Autolab PGSTAT204 potentiostat/ galvanostat for electrochemical characterisation of the Pt/YSZ system under 'non-reactive' conditions with only CO_2 flow and also under 'reactive' conditions with both CO_2 and H_2 gas flow on samples with and without alkali metal deposition. In this case, the alkali metal i.e. sodium (Na) was deposited dropwise using 2μL of NaOH solution (Merck) at different concentrations (1.5×10^{-4}, 6×10^{-4} and 0.003M) on the projected Pt surface area of 56cm^2 to produce 0.32, 1.6 and 8% coverage respectively. The Na coverage shown in Table 1 was calculated based on the assumption that there are 10^{15} Na atoms (with circular shape) in a monolayer coverage of Pt [17].

Table 1. Sodium loading and percentage of sodium coverage

NaOH (M)	Na (10^{15} atom)	Na/Pt (10^{14} atom/cm^2)	% Na coverage deposited	Cumulative % Na coverage
1.5×10^{-4}	0.18	0.03	0.32	0.32
6×10^{-4}	0.72	0.16	1.29	1.62
0.003	3.61	0.81	6.46	8.08

The cyclic voltammetry operating conditions (e.g. scan rate, and partial pressures) were manipulated to obtain information concerning the state of species adsorbed on the Pt/YSZ. The scan rate commonly used in this experiment was 100mVs^{-1} except when varying scan rates between 50 to 100mVs^{-1}. The presence of surface species has high dependency on the scan rate as the magnitude of the increase in reduction peak greatly depends on the period of the experiment [18]. The temperature was kept constant at 350°C, while the partial pressure of CO_2 was set at 1kPa except for the study of varying scan rates which was conducted at 3 kPa. The partial pressures of H_2 were also varied between 1-20kPa, while the total gas flow rate was maintained at 200mL/min throughout the whole study.

The catalyst surface morphology was analysed using field emission scanning electron microscopy (FESEM) (FEI Nova NanoSEM 450) manufactured by Oxford Instruments for elemental analysis.

Results and discussion

Surface Morphology

Figure 1 shows the scanning electron micrographs using FESEM at 10,000x magnification of (a) fresh and (b) used Pt catalyst taken after several cyclic voltammetry measurements under non-reactive and reactive conditions.

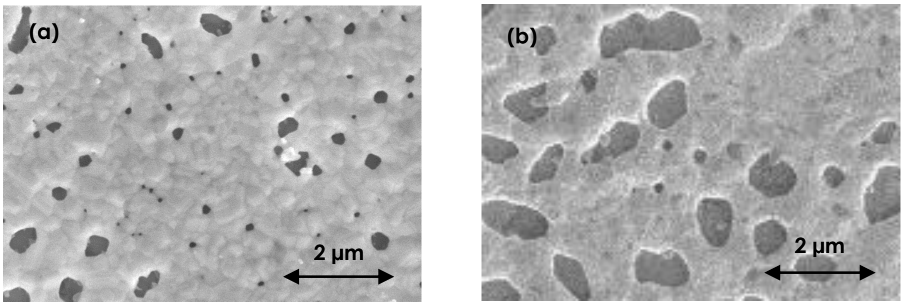

Fig. 1. FESEM images of (a) fresh and (b) used Pt/YSZ at 10,000× magnifications

After exposure to experimental conditions (up to 450°C), it can be seen that the Pt film is still continuous, but the structure became irregular with some film discontinuity. Lesser grains were observed since Pt tends to agglomerate after several experiments of cyclic voltammetry as previously observed by Jaccoud et al. [19].

CV of Pt under non-reactive conditions

Non-reactive condition in this work refers to the experimental condition with only CO_2 gas supplied. Figure 2 shows the influence of varying potential scan rates from 50 to $100mVs^{-1}$ on the features of nominally 'clean' Pt cyclic voltammogram obtained within the overpotential between working and reference electrode (V_{WR}) of 0.5 and -0.7V under flow of 3kPa CO_2. Two unsymmetrical peaks; i.e. a distinct cathodic peak (forward scan) and a poorly defined anodic peak (reverse scan) can be observed on the voltammogram. The cathodic peak can be assigned to the reduction of Pt-CO_2 complex or Pt-CO_2 derived intermediates (Pt-CO and Pt-O), while the anodic peak refers to the re-formation of the species reduced in the cathodic step. The anodic peak is much smaller than the other may be due to evolution of CO_2 or CO from the Pt surface.

The peak features show characteristic of an irreversible process with the change in scan rate, in which increasing the scan rate causes an increase in both peaks' current intensity (peak height, I_{pc}) and causes a shift in the cathodic peak potential, E_{pc} towards more negative potentials, while the anodic peak, E_{pa} shifts towards more positive potential. This indicates that the kinetics of the reaction are 'slow' and thus equilibria are not established rapidly in comparison to the voltage scan rate [20]. Larger cathodic and anodic peaks are observed with higher scan rate as the diffusion layer does not grow much further than with lower scan rate, thus more electroactive species could be measured at the tpb. It is also possible that the peaks are mainly attributed to Pt-O and the reductive as the CV features are similar to that of Pt-O [12].

Figure 3 shows that the peak current is proportional to the square root of scan rate, indicating that a diffusion-controlled electrochemical process occurs, in which the adsorbed species contribute to the reaction [21]. As mentioned earlier, with the use of YSZ, an oxygen ion conductor as solid electrolyte, the cathodic peak could also be associated to the backspillover of O^{2-} ions from the solid electrolyte, YSZ to the Pt catalyst under influence of the applied potential, and thus the small anodic peak could be contributed by O^{2-} ions migrating from the catalyst to the solid electrolyte.

Figure 4 shows the features of Pt cyclic voltammogram when modified with sodium (Na) at varying coverage (0.32-8%) under non-reactive conditions. At low Na coverage (0.32%), although the 2-peak (cathodic and anodic) voltammogram features are still similar to 'clean' Pt, the cathodic peak was observed to shift from -0.21V towards more positive potential (-0.11V) and the current hysteresis has increased in intensity. Further increase in the Na coverage to 1.6% sharply increased the anodic current at 0.5V cathodic peaks and shifted the cathodic peak to -0.18V. In our previous work on Pt(O_2)/YSZ system, similar positive shift in the cathodic peak potential was observed at low Na coverage, followed by negative shifts with increasing Na coverage [16].

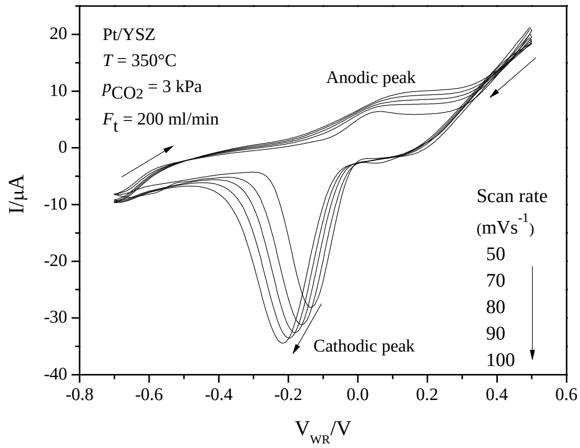

Fig. 2. The features of Pt cyclic voltammogram of 'clean' Pt films deposited on YSZ pellet at difference scan rates

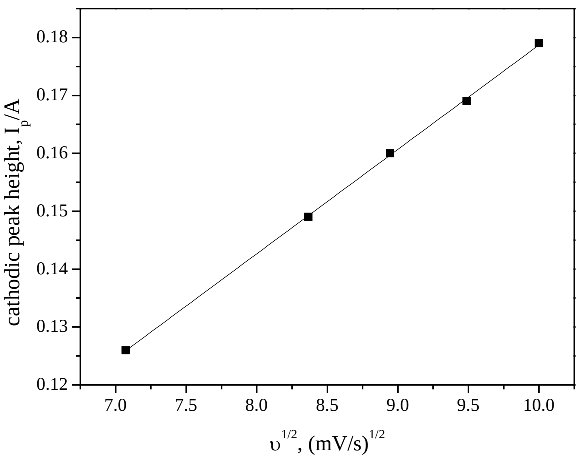

Fig. 3. Relationship between cathodic peak height, I_{pc}/A, and square root of the scan rate, $\upsilon^{1/2}$

The appearance of cathodic peaks in these voltammogram could be related to the species formed on the surface of the catalyst due to Na addition and when the oxygen ions through the electroactive support migrate to the catalyst interface and react with CO_2 and/or Na (which may be in the form of oxides or carbonates [16, 22]. On the return sweep, the presence of anodic peak with increasing overpotential and could be related to the decomposition of these reductive species on the tpb [23]. Increasing Na coverage (from 1.6 to 8%) however caused the anodic peak to disappear.

Based on the result, it can be seen that low Na coverage appear to have positive effect to the charge transfer reaction under flow of CO_2 as more prominent cathodic peak can be observed compared to broader peak seen at higher Na coverage. This finding is similar to previous work on Pt/YSZ under O_2 flow which concluded that at low sodium coverage ($<10^{14}$ atoms cm^{-2} Na/electrode area), sodium species occupied the tpb sites and reduced the charge transfer rate, while at medium coverage (10^{14}-10^{16} atoms cm^{-2} Na/electrode area), Na species spread away from the tpb to the platinum surface thus increasing the charge transfer rate and at high sodium coverage (≥10^{16} atoms cm^{-2} Na/electrode area) a build-up of sodium species both on the catalyst surface and the tpb results in a new decline of the charge transfer [16].

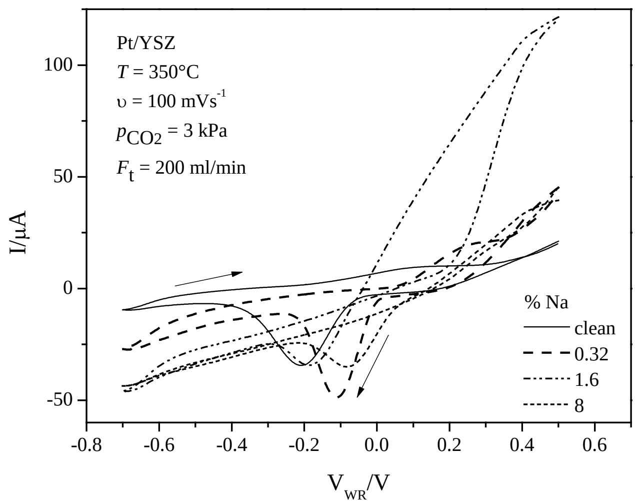

Fig. 4. Pt cyclic voltammogram of Na-modified Pt/YSZ at different Na coverage

CV of Pt/YSZ under flow of CO_2 and H_2

The CV measurements under reactive conditions refer to the conditions where CO_2 and H_2 were both added as reactants for CO_2 hydrogenation which is expected to produce methane through the methanation reaction (Equation 13) and carbon monoxide through the reverse water gas shift reaction (Equation 14) [24–27].

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O, \Delta H = -165 \text{ kJ/mol} \quad (13)$$

$$CO_2 + H_2 \rightarrow CO + H_2O, \Delta H = 41.1 \text{ kJ/mol} \quad (14)$$

In this case, the CV measurements were investigated at $100mVs^{-1}$ with varied H_2 partial pressure from 1 to 20kPa, while CO_2 partial pressure was fixed at 1kPa. As can be seen in Fig. 5, only a small cathodic peak appears during the forward scan on the nominally 'clean' Pt cyclic voltammograms, at approximately -1V under flow of 5 and 10kPa H_2, due to fast scavenging of reductive species by hydrogen in CO_2 hydrogenation reaction, producing gaseous products of CH_4 and H_2O other than CO or CO_2 which were also released from the interfacial site. This small peak is also decreasing from 10kPa onwards and completely disappears at 20kPa H_2 in excess hydrogen.

At 1kPa H_2, (H_2-deficient), it can be observed that the initial anodic current at 2V is at steady state of approximately 0µA. However, when the H_2 partial pressure was increased to 5kPa (near stoichiometry for methanation) and 10kPa (rich in H_2), current hysteresis can be observed to increase, indicating the charging of the interface possibly due to formation of more intermediate species for methanation reaction. At H_2 partial pressures of 15 and 20kPa which are very much in excess of the stoichiometric condition, easier gaseous products (CH_4 and H_2O) formation can be expected, thus less intermediate surface species are left on the Pt surface, causing less charging and the voltammogram to change towards similar features of the H_2-deficient condition. In the reverse sweep, there is flat, steady current, with a sudden increase of current at anodic potentials that gradually decreased to the initial current. The anodic current hysteresis ca. 1V shows similar trend with that seen on the cathodic side with regards to the increase in H_2 partial pressure.

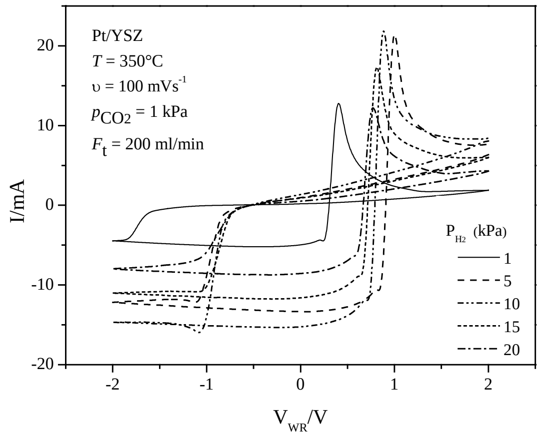

Fig. 5. Effect of varied H_2 partial pressure on cyclic voltammogram of 'clean' Pt films under reactive conditions

CV of sodium-modified Pt under reactive conditions

When the Pt catalyst was modified with sodium (Na) impregnation at varying coverage from 0.32 to 8% Na, different cyclic voltammogram features can be observed in Fig. 6 compared to the 'clean' Pt under 20kPa H_2. It can be seen that with Na addition, the initial current at V_{WR} = 2V became constant around 10μA. The 'clean' sample underwent steeper deceleration at the on-set reduction potential of around -0.7V, however the reduction curves are less steep for the Na-modified samples as the maximum current hysteresis are reduced by half than that of the 'clean' sample.

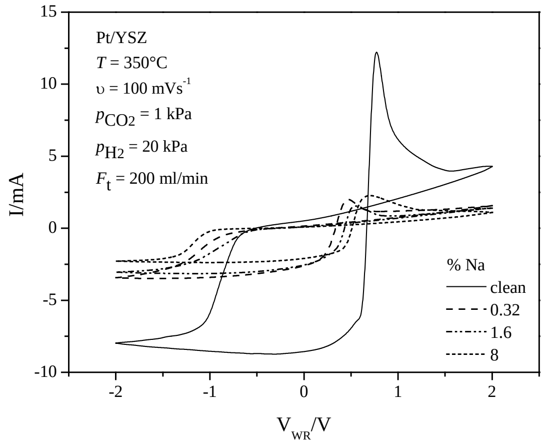

Fig. 6. Effect of sodium loadings on cyclic voltammogram of Pt under reactive conditions

In Figure 6, no clear cathodic peak can be observed on all 'clean' and Na modified samples as addition of Na may have either promoted easier formation and evolution of products as previously discussed for reactive conditions with high H_2 partial pressures. In a CV study conducted on Ru catalyst supported on K-β"-Al_2O_3 under CO_2 hydrogenation reactions at slower scan rate (10mVs^{-1}), a small cathodic peak was observed around -0.65V under flow of 14kPa H_2 [28]. At higher Na coverage (8%), a decrease in the current hysteresis and a shift in the on-set reduction potential towards more negative potential can be observed. This could be due to the strong binding between the Pt-CO_2 derived intermediates or spiltover oxygen species with Na added on the Pt surface, possibly by formation of carbonates or oxides as previously discussed under non-reactive conditions. Sodium carbonate may also block some of the tpb sites causing the rate of charge transfer reaction to decrease and become slower. Filkin et al. addressed that moderate sodium loading will enhance the chemisorption and until quite negative catalyst potentials, the metal catalyst surface will be deactivated by excessive accumulation of sodium compound [29].

Conclusions

The electrochemical reaction of CO_2 reduction and CO_2 hydrogenation over Pt/YSZ catalyst are irreversible, with sluggish electron exchange compared to the voltage scan rate under study. Under non-reactive conditions, the Pt cyclic voltammogram was found to exhibit cathodic reduction peak, which changes with addition of Na at different coverage. Under reactive conditions, the voltammogram features indicated that reduction of the surface Pt-CO_2 derived intermediates/complexes could be enhanced by sodium addition at low coverage, thus low Na coverage (<1%) was expected to promote the methanation reaction electrochemically. However, further increase in Na coverage (up to 8%) decreased the current hysteresis of the voltammogram as the catalyst surface and electroactive sites (tpb) may be predominantly occupied by Na surface species in the form of oxides/carbonates species, resulting in less favourable electrochemical activity. This study indicates that Na surface species could promote CO_2 methanation reaction which is one of the promising routes for low carbon biogas utilisation and conservation of carbon sources.

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