Electrocatalytic oxidation of methanol and carbon monoxide at platinum in protic ionic liquids

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1. Introduction

The oxidation of methanol in water using Pt electrocatalysts is the anode reaction in direct methanol fuel cells (DMFCs) and is a complex reaction involving the transfer of six electrons and six protons:

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \]  

(1)

The formation of adsorbed intermediates such as CO on the Pt surface results in a methanol oxidation overpotential of several hundred millivolts that reduces the efficiency of DMFCs [1,2]. One approach to solving the problem of Pt poisoning is to include into the catalyst a metal such as Ru, which readily forms surface oxides that can facilitate the complete oxidation of CH$_3$OH to CO$_2$ [3]. Alternatively, one can raise the temperature, T, of the cell but the Nafton® membranes usually used in DMFCs must be hydrated to conduct protons. Consequently, T is usually kept below 100 °C to ensure the presence of liquid H$_2$O in the electrolyte [4,5].

A particularly promising approach towards the development of fuel cells operating above 100 °C is to use protic ionic liquid (PIL) electrolytes, which can conduct protons in the absence of liquid water and have very low vapour pressures. PILs have been used as electrolytes in H$_2$ fuel cells and remarkably high rates of O$_2$ reduction and H$_2$ oxidation have been observed at elevated T [6]. The high rates of O$_2$ reduction in PILs are particularly promising, generating open circuit potentials (OCPs) exceeding that achievable in conventional H$_2$-fuelled polymer electrolyte membrane fuel cells containing hydrated electrolytes [8].

The aim of this work is to explore the feasibility of using PILs as electrolytes for DMFCs. If CH$_3$OH oxidation does occur rapidly above 100 °C in PILs, it is possible that an efficient DMFC could be built with a higher OCP than that of conventional DMFCs. We studied CH$_3$OH oxidation electrocatalysis at Pt in diethylmethylammonium trifluoromethanesulfonate, [dema][TfO], which was chosen because O$_2$ reduction occurs rapidly in this liquid [6]. After discussing the electrochemistry of [dema][TfO] at Pt electrodes as a function of T (and in particular the role of trace H$_2$O oxidation at the Pt electrode), we describe the oxidation of CO$_2$ at Pt in [dema][TfO]. These observations are then correlated with observations made during the oxidation of CH$_3$OH, allowing us to study the role of CO and H$_2$O during CH$_3$OH oxidation in this PIL. Finally, we discuss the prospects for the use of PIL electrolytes in DMFCs and make some recommendations for the development of protic ionic liquid electrolyte fuel cells and these implications are discussed.

**Abstract**

Oxidation of H$_2$O, CO and CH$_3$OH was investigated at Pt as a function of temperature in the protic ionic liquid diethylmethylammonium trifluoromethanesulfonate. Trace H$_2$O oxidation in the ionic liquid results in coverage of the Pt with adsorbed oxides. Increasing the temperature significantly reduces the potential at which this reaction occurs. CH$_3$OH and CO oxidation kinetics increased significantly with increasing temperature and oxidation of each species coincided with coverage of the Pt surface by the oxide. These observations indicate that surface oxides are required for complete oxidation of CH$_3$OH to CO$_2$ in the protic ionic liquid, in a similar way to that observed in conventional aqueous electrolytes. While the overpotential for CH$_3$OH oxidation was drastically higher than that observed in purely aqueous electrolytes, it decreased with increasing water content of the ionic liquid. The results described here have implications for the development of protic ionic liquid electrolyte fuel cells and these implications are discussed.

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2.2. Electrochemical measurements

The sealed electrochemical cell contained a 2 mm diameter Pt disk working electrode, a Pt flag counter electrode and Ag/Ag+ reference electrode, which was constructed by immersing an Ag wire in 10 mM [Ag][TfO] in [dema][TfO]. Controlled \(T\) measurements were performed by immersing the entire cell in an oil bath on a hot plate. The Pt disk electrode was polished using an aqueous suspension of 0.05 μm alumina on a felt polishing pad, cleaned ultrasonically in water, rinsed with water and dried under Ar.

Prior to use, the electrochemical cell was charged with ~5 mL of [dema][TfO] and dried overnight. CO stripping experiments were performed by first holding the potential of the Pt electrode at 0.1 V vs. Ag/Ag+ in CO-saturated [dema][TfO] for 10 min. The PIL was then purged of CO by bubbling with Ar for 30 min (while holding the Pt electrode at 0.1 V) and CO was stripped from the Pt surface during an anodic potential sweep. CH₃OH oxidation experiments were performed after addition of the appropriate amount of CH₃OH and/or H₂O to the cell (see below for further details) while under an Ar atmosphere. Hydrodynamic voltammograms were obtained by vigorously stirring the PIL with a magnetic stirrer bar while sweeping the potential of the working electrode.

3. Results and discussion

3.1. Electrochemistry of [dema][TfO] at Pt

Fig. 1A shows a series of cyclic voltammograms (CVs) obtained at a Pt electrode in [dema][TfO] in the range —0.2 V to 1.8 V. The anodic peaks between 0.5 and 1.0 V were due to oxidation of trace H₂O in the PIL resulting in the formation of an adsorbed oxide layer on Pt, which we call Pt–OHads, and the cathodic peaks were due to reduction of Pt–OHads to Pt [7,10]:

\[
\text{Pt} + \text{H}_2\text{O} \rightarrow \text{Pt–OH} + \text{H}^+ + e^- (2)
\]

The appearance of this process demonstrates that, even after heating the PIL under vacuum at 70 °C for 48 h and isolating the cell from the atmosphere, the concentration of trace H₂O (244 ppm) was sufficient to cause the formation of an adsorbed oxide on the Pt surface. The peak-to-peak separation for OHads formation/removal was especially large at low \(T\), suggesting that Pt–OHads formation/removal was slow. However, as \(T\) increased, the peak-to-peak separation decreased, demonstrating that the Pt–OHads formation/removal was activated with increasing \(T\).

3.2. CO oxidation in [dema][TfO]

In conventional aqueous electrolytes, CH₃OH oxidation to CO₂ involves a surface reaction between adsorbed OHads, which forms due to H₂O oxidation (Eq. (2) above), and adsorbed methanol oxidation products. The most recalcitrant poisoning species is COads and complete oxidation of COads to CO₂ occurs via reaction with OHads [3]:

\[
\begin{align*}
\text{Pt} + \text{CH}_3\text{OH} &\rightarrow \text{Pt–CO}_\text{ads} + 4\text{H}^+ + 4e^- (3) \\
\text{Pt–CO}_\text{ads} + \text{Pt–OH}_\text{ads} &\rightarrow 2\text{Pt} + \text{CO}_2 + \text{H}^+ + e^- (4)
\end{align*}
\]

To investigate whether a similar mechanism occurs during oxidation of CH₃OH in [dema][TfO], the electrochemistry of CO was studied at Pt. Fig. 1B shows linear sweep voltammograms obtained during stripping of COads from Pt in [dema][TfO] at a series of temperatures. When the potential was scanned in a positive direction at each temperature, an anodic peak was observed, which we attribute to oxidation of COads on the Pt surface. Fig. 1B shows that, as \(T\) increased, the stripping peak narrowed and moved to more negative potentials. It is possible that changes in the adsorption mode of CO on the Pt surface (a factor that has yet to be studied in PILs) could be responsible for the observed behaviour. However, this is unlikely as the potential was controlled during pre-concentration of CO on the Pt surface. Furthermore, the shift in the CO oxidation onset as \(T\) increased mirrored the shift in the wave due to OHads formation in Fig. 1A, suggesting that COads oxidation only occurred in the PIL when the Pt surface was covered with OHads. This behaviour is similar to that observed in aqueous electrolytes, given by Eq. (4).

3.3. CH₃OH oxidation in [dema][TfO]

Fig. 2A shows a series of CVs obtained at a Pt electrode in [dema][TfO] containing 0.5 M CH₃OH. In each case, a broad peak was observed during the forward sweep and comparison of these CVs with the blank CVs (Fig. 1A) demonstrates that the peaks were solely due to CH₃OH oxidation in [dema][TfO]. During the negative sweep, the current rapidly decayed to a negligible value until a potential of approximately 0.2 V, when a small anodic peak appeared that increased in height with increasing \(T\) (Fig. 2A inset). The anodic peak appeared at the potential where Pt–OHads removal from the Pt surface occurred (Fig. 1A), suggesting that, during the negative sweep, CH₃OH oxidation restarted as some OHads was removed from the surface [11].
words, it appears that the availability of $\text{OH}_{\text{ads}}$ on the Pt surface governs the onset potential for complete $\text{CH}_3\text{OH}$ oxidation. To investigate the role of $\text{H}_2\text{O}$ oxidation in $\text{CH}_3\text{OH}$ oxidation in [dema][TfO] further, hydrodynamic voltammograms were recorded in [dema][TfO] containing $\text{CH}_3\text{OH}$ and varying amounts of $\text{H}_2\text{O}$ (Fig. 2B). It is clear that adding successively higher concentrations of $\text{H}_2\text{O}$ to the PIL resulted in a progressive shift of the $\text{CH}_3\text{OH}$ oxidation wave to less positive potentials. This result demonstrates that $\text{CH}_3\text{OH}$ oxidation becomes more facile as the $\text{H}_2\text{O}$ content of the PIL increases, which is presumably due to the increased coverage of the Pt surface with $\text{OH}_{\text{ads}}$ at lower potentials as the concentration of $\text{H}_2\text{O}$ increased [10]. This result could have implications for the development of DMFCs containing PIL electrolytes. On one hand, the use of PILs allows one to access higher $T$ and enhance $O_2$ reduction kinetics at the cathode. On the other hand, our results demonstrate that loss of $\text{H}_2\text{O}$ from the electrolyte will result in a large overpotential for $\text{CH}_3\text{OH}$ oxidation that will reduce the cell performance. In separate measurements, we have measured the potential at which $\text{H}_2$ oxidation occurs in [dema][TfO] [7], which corresponds to a potential of $-0.63 \text{ V vs. Ag/Ag}^+$, demonstrating the very high overpotential for $\text{CH}_3\text{OH}$ oxidation in [dema][TfO], even in PIL solutions containing up to 3 M $\text{H}_2\text{O}$ (Fig. 2B).

One possible solution to this problem of high overpotential for $\text{CH}_3\text{OH}$ oxidation in [dema][TfO] is to use alloy electrocatalysts such as PtRu, which should lower the potential for $\text{OH}_{\text{ads}}$ formation. As our work also shows, increasing $T$ will probably not reduce the effects of poisoning of protic ionic liquid electrolyte fuel cell anodes with CO from $\text{H}_2$ fuel supplies (Fig. 1B) and it is likely that the use of PtRu catalysts will also aid in mitigating such poisoning.

4. Conclusions

The electrochemical oxidation of CO and $\text{CH}_3\text{OH}$ has been studied at Pt electrodes in the protic ionic liquid [dema][TfO]. Our results demonstrate that oxidation of trace $\text{H}_2\text{O}$, which is unavoidably present in this liquid, provides the adsorbed oxygen species necessary for complete oxidation of $\text{CH}_3\text{OH}$. However, our results suggest that catalyst deactivation occurs readily in this liquid and that the overpotentials for both CO oxidation and $\text{CH}_3\text{OH}$ oxidation are very large. Future work in our group will focus on studying the electrochemical stability of Pt catalysts in protic ionic liquids. In addition, the inclusion of readily oxidised metals such as Ru to the Pt catalyst may aid in reducing the overpotential for methanol oxidation and we are currently exploring this possibility.

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