ELECTROCHEMICAL REDUCTION
OF CARBON DIOXIDE INTO FORMATE

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Abstract

The electrochemical reduction of CO_2 dioxide into $HCOO^-$ on a Sn cathode is well described in literature. However, the issue of deactivation and loss of Sn and a suitable non-aqueous supporting electrolyte remains unresolved. This work aims to develop and characterize Sn as a cathode material and describe a suitable non-aqueous supporting electrolyte for CO_2 solvation. A Sn plated glassy carbon rotating disc is the cathode, and Pt wire as the anode. The catholyte to be investigated are H_2O and CH_3OH while the anolyte will remain as KOH. The reactor is batch type with separation of the catholyte and anolyte achieved using a Nafion membrane. CO_2 gas will be bubbled into the catholyte and reduced at the Sn plated cathode. Linear sweep voltammetry with a maximum potential of -1.5 V vs. SHE is to be carried out on the system. Results will then be analysed and compared with past works by other authors. Acquired data will be used to elucidate the efficiency of the Sn electrode in the reduction of CO_2, the effects and extent of the cathode degradation and the solvent type in the reduction of CO_2. At completion, this work is able to describe the optimal conditions for electrochemical reduction of CO_2 into $HCOO^-$ within the scope of study.

Keywords: Electroreduction, Electrolyte, $HCOO^-$.

1. Introduction

Electrochemical reduction of CO_2 can valorise CO_2 into $HCOO^-$ on a Sn electrode, Eq. (1).

$$CO_2 + H^+ + 2e^- \rightarrow HCOO^- \tag{1}$$

$HCOO^-$ requires relatively little energy to form and can be converted with high Faradaic efficiencies [1]. The process first requires $CO_{2(g)}$ or $CO_{2(aq)}$ to be

Subscripts	
ad	Adsorbed
aq	Aqueous
g	Gas
l	Liquid
Abbreviations	
DMF	Dimethylformamide
SHE	Standard hydrogen electrode

adsorbed onto the Sn electrode. Electricity is used to supply electrons for the reduction process of the $CO_{2(ad)}$ to $CO_{2(ad)}{}^{.-}$. The radical anion then undergoes protonation to form $HCOO^{.}$. The $HCOO^{.}$ radical then receives another electron to form $HCOO^-$ and desorbs into the electrolyte [2].

The objectives of this project are to develop Sn as a catalyst to reduce CO_2 into $HCOO^-$ and to study the effects of electrolyte type on the reduction process. The electrochemical reduction of CO_2 is affected by three major factors; the cathode, the transport of CO_2 to the cathode, and the potential applied.

The choice of catalyst, together with the supporting electrolyte type determines the type of product obtained. $HCOO^-$ can be produced from 80% to as high as near 100% faradaic efficiency by using In, Sn, Hg, and Pb cathodes [3]. These elements have high H_2 overpotential and will hence suppress competing H_2 evolution. Sn is chosen for our work as it is readily available, relatively inexpensive and not as toxic compared to Hg or Pb. However, gradual deactivation of Sn with operation time due to catalyst poisoning have been reported in literature [4, 5].

H_2O is an abundant resource for CO_2 solvation. In an aqueous electrolyte, CO_2 exist in three forms, $CO_{2(ad)}/H_2CO_3$, $HCO_3{}^-$, and $CO_3{}^{2-}$, Eqs. (2), (3) and (4).

$$CO_{2_g} + H_2O_l \leftrightharpoons H_2CO_{3_{aq}} \tag{2}$$

$$H_2CO_{3_{aq}} \leftrightharpoons H^+{}_{aq} + HCO_3{}^-{}_{aq} \tag{3}$$

$$HCO_3{}^-{}_{aq} \leftrightharpoons H^+{}_{aq} + CO_3{}^{2-}{}_{aq} \tag{4}$$

The concentration of each species present is dependent on the pH of the electrolyte. Above pH 8.3, the carbon exist as $CO_3{}^{2-}$. Between pH 8.3 and pH 4.5, the carbon exist as $HCO_3{}^-$. Below pH 4.5, the carbon exist as CO_2/H_2CO_3 [6].

The species that actively takes part in the reduction process is the $CO_{2(ad)}/H_2CO_3$ [2]. H_2CO_3 may also decompose into CO_2 and proceed to be reduced at the cathode, Eq. (5), however this process is too slow for it to be practical [2].

$$HCO_3{}^- \rightarrow CO_2 + OH^- \tag{5}$$

Lowering the pH of the electrolyte can dissolve more CO_2/H_2CO_3 and hence improve mass transport to the cathode. However, a lower pH causes H_2 evolution to be more prevalent [2]. There is still disagreement between researchers on the optimal pH for the electrolyte. Whipple (2010) used a single electrolyte, KOH and found that lowering the pH increases selectivity of the Sn catalyst as noted in the increase in its faradaic efficiency [7]. However, Innocent et al. (2008) found that best conditions for $HCOO^-$ production in his experiment set is achieved by using 0.5 M NaOH catholyte set at pH of 8.6 by bubbling CO_2 through [8].

Non-aqueous electrolytes do not normally contain H^+ and hence cannot evolve H_2. However H^+ is still a necessary ion for the formation of $HCOO^-$ and at least 1000 mmols of H_2O must be added to provide the H^+ ion sufficiently to selectively evolve $HCOO^-$ [2].

A mixture of non-aqueous electrolytes and H_2O offer the advantage of control over the available H^+ ion and hence control over H_2 evolution. The non-H_2O component of the solution can dissolve CO_2 more readily compared to a pure H_2O configuration. CH_3OH is able to dissolve 138 mmol/l of CO_2, compared to 34 mmol/l of CO_2 for H_2O at room at 298 K [9].

$CO_2^{\cdot-}$ formation is the rate determining step of the entire chain [2]. Potentials for CO_2 adsorption on the electrode, formation of subsequent intermediates other than $CO_2^{\cdot-}$ and final products are negligible. The formation of $CO_2^{\cdot-}$ has a standard potential of -1.85 V vs SHE in aqueous electrolyte, or -1.98 V vs. SHE in DMF [2].

H_2 evolution is a major side reaction that accompanies CO_2 reduction in an aqueous electrolyte. The H_2 evolution can be written as Eqs. (6), (7) and (8).

$$H^+ + e^- \rightarrow H_{ad} \tag{6}$$

$$H_{ad} + H_{ad} \rightarrow H_2 \tag{7}$$

$$H^+ + e^- + H_{ad} \rightarrow H_2 \tag{8}$$

Other than the evolution of H_2 gas, Hori claims that H_{ad} deactivates the $CO_2^{\cdot-}$ radical to CO_{ad}, Eq. (9) [2].

$$CO_2^{\cdot-} + H_{ad} \rightarrow CO_{ad} + OH^- \tag{9}$$

This in conflict with Li who claim H_{ad} is beneficial and reacts with $CO_2^{\cdot-}$ to form $HCOO^-$, Eq. (10) [3].

$$CO_2^{\cdot-} + H_{ad} \rightarrow HCOO^- \tag{10}$$

2. Methodology

A Sn plated glassy carbon rotating disc is the cathode, and Pt wire is the anode. The catholyte to be investigated are H_2O and CH_3OH while the anolyte will remain as KOH. The reactor is batch type with separation of the catholyte and anolyte achieved using a Nafion membrane. A selective permeable membrane separating the anode and cathode chambers stops the oxidation of

the newly reduced $HCOO^-$ back into CO_2 and the reduction of O_2 into OH^-, Eqs. (11) and (12).

$$HCOO^- \rightarrow CO_2 + H^+ + 2e^- \tag{11}$$

$$O_2 + H_2O + 4e^- \rightarrow 4OH^- \tag{12}$$

CO_2 gas will be bubbled into the catholyte and reduced at the Sn plated cathode. The effect of pH on the performance of the system is investigated. Linear sweep voltammetry carried out on the system. The electrode is rotated at 600 rpm to improve mass transport. Prior to each set of experiment, the remaining Sn will be stripped off first and then re-deposited under the same conditions to ensure the thickness of the Sn layer for each run is similar. The catholyte is first purged with N_2 to remove unwanted dissolved gasses. CO_2 is bubbled into the catholyte for 30 minutes and then continuously throughout the experiment.

In experimental runs requiring the manipulation of pH, 20 Grade C buffer solutions of pH 5.00, pH 7.00, and pH 9.00 Centipur® are used as it is in place of H_2O.

The H_2O electrolyte is replaced with aqueous 50% AR grade CH_3OH to investigate the advantages of using CH_3OH to improve mass transport to the cathode. The H_2O component in the aqueous 50% CH_3OH is important as a source of H^+ in the formation of $HCOO^-$.

The obtained linear sweep voltammgram are analyzed by comparing the area under the curve for the N_2 and CO_2 species and by observing the onset potential of CO_2 reduction.

3. Results and Discussion

Reduction of CO_2 can be observed from Figs. 1 to 4 by noting that the CO_2 curve drops faster than the curve for our baseline case, an electrolyte solution saturated with N_2. According to W. Li, 2010, the product was $HCOO^-$ as Sn cathodes are highly selective for $HCOO^-$ production [3]. In the experiment conducted with H_2O as an electrolyte, H_2 evolution had not initiated or is minimal due to the low potential applied.

The best pH found for CO_2 reduction is found to be pH 9. Onset reduction potential for pH 9 is found to be the lowest, circa -1.2 V vs SHE, versus circa -1.3 V for pH 7 and circa -1.4 V for pH 5. At pH 9, current density for CO_2 reduction was 6.5 Am^{-2} at applied potential of -1.5 V. At pH 7, current density was 4.5 Am^{-2} and for pH 5, 3.5 Am^{-2}. At pH 9, total charge that went into the reduction of CO_2 was 0.111 C. At pH 5, total charge estimated is 0.040 C and for pH 7, 0.045 C.

In Fig. 3, a peak exists at -1.1 V for the N_2 curve and at -0.9 V for the CO_2 curve. This is attributed to the formation of SnO_x which is beneficial to the formation of $HCOO^-$ [10].

In Fig. 4, CH_3OH was added to improve CO_2 solubility. The onset CO_2 reduction potential was circa -1 V vs SHE. Current density for CO_2 reduction is lower than that for H_2O, about -3.0 Am^{-2} at an applied potential of -1.5 V. This is due to a relatively high current density of -5.0 Am^{-2} of an indentified

competing reduction occurred starting from circa -1.3 V. Reduction of CH_3OH itself is ruled out as CH_3OH is still stable for CO_2 reduction in that range. H_2 evolution is also unexpected because otherwise the N_2 curve would be similar to that for Figs. 1, 2, and 3. Total charge that went into the reduction of CO_2 is only 0.016 C.
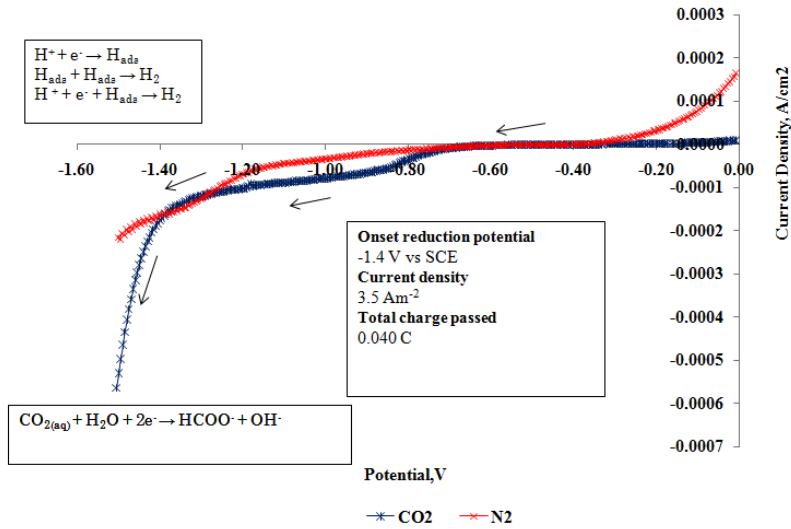
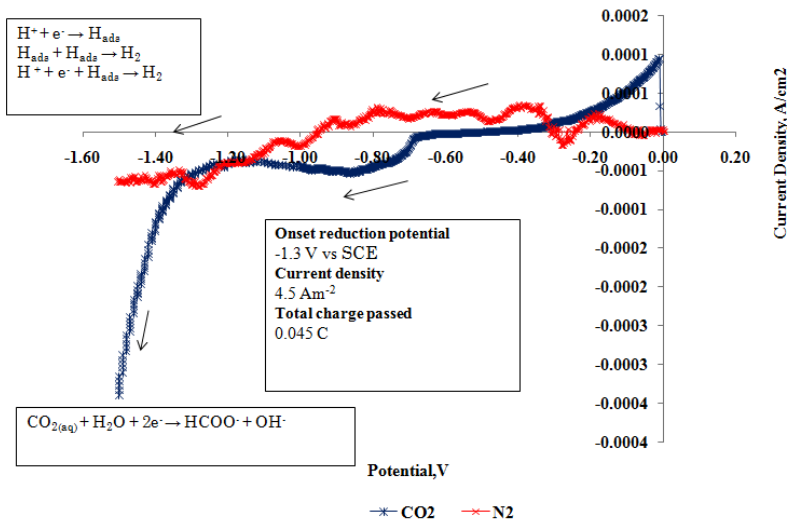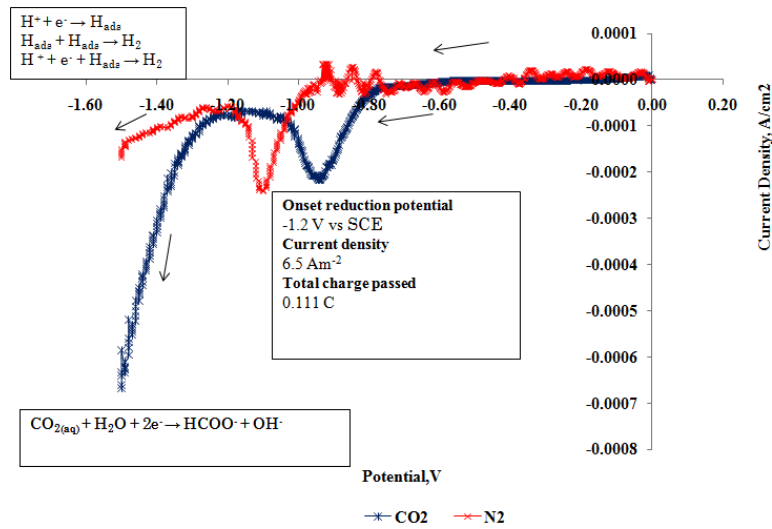Fig. 1. Reduction of CO_2 in pH 5 H_2O.

Fig. 2. Reduction of CO_2 in pH 7 H_2O.

$H^+ + e^- \rightarrow H_{ads}$
$H_{ads} + H_{ads} \rightarrow H_2$
$H^+ + e^- + H_{ads} \rightarrow H_2$

Onset reduction potential
-1.2 V vs SCE
Current density
6.5 Am^{-2}
Total charge passed
0.111 C

$CO_{2(aq)} + H_2O + 2e^- \rightarrow HCOO^- + OH^-$

Fig. 3. Reduction of CO_2 in pH 9 H_2O.

$H^+ + e^- \rightarrow H_{ads}$
$H_{ads} + H_{ads} \rightarrow H_2$
$H^+ + e^- + H_{ads} \rightarrow H_2$

Onset reduction potential
-1.0 V vs SCE
Current density
3.0 Am^{-2}
Total charge passed
0.016 C

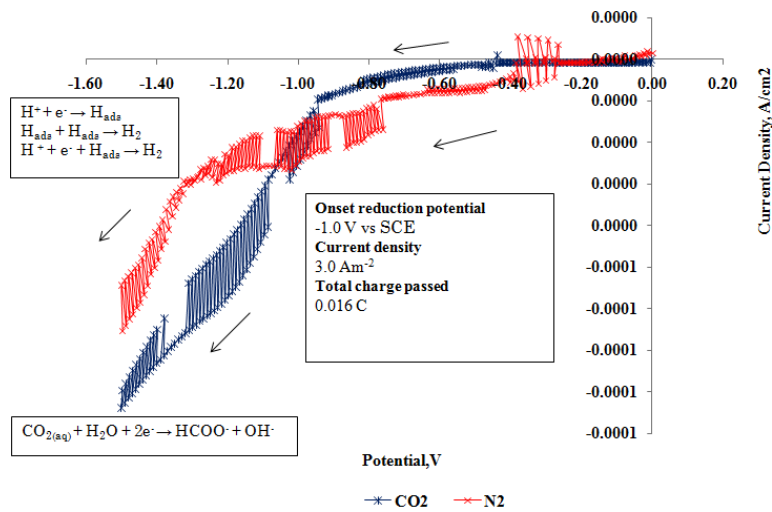$CO_{2(aq)} + H_2O + 2e^- \rightarrow HCOO^- + OH^-$

Fig. 4. Reduction of CO_2 in aqueous CH_3OH 50%.

The noise observed in the graphs is likely due to the bubbling CO_2 disrupting ion transport to the cathode and/or reduction of impurities in the electrolyte. It is recommended that pre-electrolysis is carried out in future studies to reduce electrochemical noise.

4. Conclusions

An investigation has been made on the reduction of CO_2 to $HCOO^-$. Some concluding observations from the investigation are made. The desirable pH for CO_2 reduction is in the basic region. A higher pH means that in the more carbonate species, i.e., HCO_3^- and CO_3^{2-}, exist instead of the electro-active species CO_2. However, the H_2 evolution is also less prevalent and more current will go towards the reduction of CO_2. Also, the basic region lowers the onset potential for CO_2 reduction. It is important that the electrolyte not be contaminated as impurities may also be reduced at the cathode consuming charge and reducing overall efficiency.

Acknowledgements

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