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Electrochemical reduction of formic acid through its decarbonylation in phosphoric acid solution

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Research Highlights
- Conversion of HCOOH to low molecular weight organics by a new pathway
- High current efficiency to methanol and acetaldehyde

Abstract

The electrochemical reduction of formic acid on a copper cathode in 85% w/w H_3PO_4 electrolyte at 70 ^0C was studied. In this electrolyte formic acid is partially decomposed to carbon monoxide and water. The experimental results showed that the formation of the products is strongly related to the presence of carbon monoxide in the solution and this suggests that CO is the key intermediate for the formation of the detected producs. At -0.45 V vs. Ag/AgCl the main products were CH_3OH and CH_3CHO with %Current Efficiency (%CE) of 27.6 and 25.8% respectively, whereas a part of the produced methanol(about 50%) was converted to methyl dihydrogen phosphate (25%) and methyl formate (21.8%). At more negative potentials than -0.5 V ethanol was produced by a maximum %CE of 7.9% at -0.75V. The electrochemical reduction of a CO saturated solution under the same conditions gave the same products albeit the %CE of methanol was lower.

Keywords: Formic acid, decarbonylation, copper, electroreduction

1. Introduction

Formic acid is one of the main products of the electrochemical reduction of CO_2 on various electrodes. Its current efficiency (%CE) is usually between10-90% depending on the metal cathode and the other electrolysis conditions [1-3]. In addition, formic acid is one of the main products of the treatment of biomass under hydrothermal conditions [4]. Thus, the conversion of formic acid into low molecular weight organics that have higher energy density and are consumed in large amounts is of great importance.

The reduction of formic acid is thermodynamically favorable [5] since its standard potential for the reduction to formaldehyde is only 0.056 V, but kinetically difficult. Literature studies since the beginning of the 20th century have shown that the rate of the reduction on many metals such as Pb, Ni, Fe, Co and Pt is very low [6]. The reduction on electrodeposited tin and on liquid Cerrolow136 [7] gives a %CE in the range 7.4-13.7% but the effective current density was only 140 $\mu A/cm^2$.

In 1977 Russell et al [8] achieved %CEs 11.9 and 99% on Pb and Sn respectively but the current density was less than 4 $\mu A\ cm^{-2}$. They found that the adsorption of HCOOH on the electrode which takes place in a narrow potential region near the potential of zero charge (pzc) may be the rate determining step. Kapusta and Hackerman [9] attributed the low rate of the reduction on tin to the formation of organometallic complexes on the tin cathode which accelerate the hydrogen evolution reaction. Cyclic voltammetry studies on many metal cathodes and TiO_2 [10, 11] showed that the current increased linearly with the concentration of formic acid but this increase was not due to the reduction of formic acid but to the acceleration of the hydrogen evolution reaction in the presence of formic acid. In a work from our laboratory [12] it was found that formic acid is reduced in acidic solution (2 M HCl) on a Cu(88)Sn(6)Pb(6) cathode and that the main products were methanol and ethanol having

%CEs of 30.3 and 37.6% respectively at -0.8 V vs. Ag/AgCl. In concentrated solutions of formic acid a noticeable amount of CH_3CHO (%CE 17.1) was also detected.

The reduction of formic acid by chemical methods is also difficult since strong reducing agents such as Cr^{+2} that can reduce dinitrogen [13] and carbon monoxide [14] are not capable to reduce formic acid. The only efficient reducing agent for formic acid is metallic magnesium in strongly acidic solution which reduces it to formaldehyde and this is a good analytical method for its determination [15].

It is well known that formic acid undergoes decarbonylation or decarboxylation under various conditions through the reactions:

$$HCOOH \rightleftarrows CO + H_2O \quad (1)$$

$$HCOOH \rightleftarrows CO_2 + H_2 \quad (2)$$

It has been proved that in the presence of some inorganic acids such as orthophosphoric and pyrophoshporic at low temperature (20-70 ^0C) the decarbonylation pathway is the dominant one [16].

The present work aims to the reduction of the produced CO from the decarbonylation reaction (1) instead of that of formic acid which is much more difficult.

2. Experimental

Formic acid (purity 98%) and H_3PO_4 85% w/w was supplied from Baker and the other chemicals from Fluka. Copper foil 99.999% was supplied from Sigma-Aldrich. The solutions were prepared using ultra pure water from a Sation9000 apparatus and the electrolyte (85% w/w H_3PO_4) was pre-electrolyzed for 4 h at -1.2 V using a carbon cloth as cathode in order to remove trace metallic impurities. The electrolyte was freshly prepared in order to avoid the decomposition of formic acid from phosphoric acid.

A Teflon cell having a total volume of 24 mL divided in two equal volume compartments by a Nafion 117 (H^+ form) cation exchange membrane was used in all electrolytic experiments. A detailed description of this cell has been given in a previous work [17].The copper cathode had a geometrical area of 1.76 cm^2. A Pt foil (Alpha Metal) having an area of 7 cm^2 was used as anode.The cell was placed in a thermostated water bath until the required temperature was achieved.

The potential was controlled by a Wenking POS 73(Bank Elektronik) potentiostat and the reference was the saturated Ag/AgCl electrode. The copper electrode was electrolytically polished by anodization in 85% H_3PO_4 and subsequently rinsed with ultra–pure water. A stream of He having a flow rate of 10 mL min^{-1} was used to withdraw the gaseous products and a part of the produced organic liquids such as methanol ethanol and acetaldehyde from the cell during the electrolysis. The escaped liquids from the cell by the gaseous stream were collected in three tubes containing cold water.

No significant volume loss of the catholyte was observed at the end of electrolysis since the liquid sample was only 1 μL.

A gas chromatograph (GC) supplied by a Plot Q 30 m, 0.530 mm and a Molecular Sieve 5A, 30 m, 0.530 mm connected in series by a three way valve and a TCD detector was used for the determination of H_2, CO and CO_2. A second gas chromatograph supplied by a Pora Plot Q 25 m, 0.53 mm column and FID detector was used for the analysis of the low molecular weight organics and hydrocarbons. The samples from the catholyte were neutralized by NaOH 5M before their injection to GC. Tests for the possible production of formaldehyde were performed by the chromotropic acid method [15].The detection limit for methane and methanol was 1 ppm and the reproducibility of the experimental results was established to be within ±5%.

The %CEs of the products were calculated by assuming that the number of electrons is 4 for CH_3OH, 8 for CH_3CH_2OH, 6 for CH_3CHO and CH_4 and 10 for C_2H_6.

3. Results and Discussion

3.1 Cyclic voltammetry

The cyclic voltammograms (Fig. 1) in 85% H_3PO_4 solution showed that at potential more negative than -0.43 V the current in presence of carbon monoxide was lower than that of the background electrolyte and this is in accordance with previous works [18,19]. The decrease in the current was attributed to the chemisorption of CO on the cathode resulting in the inhibition of the hydrogen evolution reaction. On the contrary, in the presence of HCOOH the current was higher than that of the background electrolyte. A similar behavior was observed on other cathodes such as Sn [9], Pt [10] and TiO_2, Ti, In, Ag [11] and was assigned to the acceleration of the hydrogen evolution reaction in the presence of HCOOH rather than to its reduction [11].

3.2. Influence of the potential.

In open circuit the analysis of the outgoing from the cell He stream showed that it contained 1330 ppm of CO, 80ppm of CO_2 and 75 ppm of H_2. The ratio of the concentrations of CO_2 and H_2 was about one as it is expected by the stoichiometry of the reaction (2). This amount of hydrogen which was formed by the non electrochemical reaction (2) was not taken into account in the reported %CE of H_2. As it is shown in Table 1 the main products of the reduction in formic acid containing solutions at -0.45 V were CH_3OH and CH_3CHO with %CEs 27.6 and 25.8 respectively. At more negative potentials than -0.50 V ethanol was detected with a maximum %CE of 7.9% at -0.75 V.

The % CEs of the hydrocarbons which were the main products of the reduction of CO [18-20] in our conditions were very low and reached only 2.6% at -1.05 V. During these experiments a part of CH_3OH (about 10%) passed through the membrane in the anodic compartment of the cell and after its oxidation on the anode gave traces of HCHO. A better view of the distribution of the products at various potentials is shown in Fig.2.

The observed maximum at about -0.75 V in the %CE of ethanol vs. E and the corresponding decrease in the %CE of acetaldehyde is characteristic for the intermediate product of a consecutive reaction mechanism [21] and implies that ethanol is produced by the reduction of acetaldehyde.

The calculated total %CEs deviates significantly from 100% in the experiments performed between -0.45 and -0.55 V. Under the conditions of the electrolysis the partial esterification of H_3PO_4 and HCOOH by the produced CH_3OH was possible. In order to find the decree of esterification, a 10 mL mixture of 85%H_3PO_4, 1% HCOOH and 320 ppm of CH_3OH was left to react at 70 ^0C for 2 h. The analysis of the solution showed that the unreacted methanol was 170 ppm (53%) and that 70 ppm of CH_3OH (21.8%) were converted to $HCOOCH_3$. The mass balance showed that 80 ppm of CH_3OH (25%) were converted to $CH_3H_2PO_4$. By taking into account these results it can be concluded that the %CE of CH_3OH shown in Table 1 represents about 50% of the total CH_3OH production. These findings can explain the deviation of the total %CEs from 100%. Attempts to detect other organic products by proton and ^{13}C NMR and LC-MS (positive electrospray ionization) were not conclusive due to their small concentrations. However, the presence of $CH_3H_2PO_4$ was verified by LC-MS analysis and that of $HCOOCH_3$ by direct injection of a sample from the outgoing from the cell gaseous stream to MS-electron ionization (molecular ion m/z=60 and its main fragments 31 and 29).

As it is shown in Fig.3 the current density was almost constant during the electrolysis and this means that that the copper electrode was not deactivated by adsorbed organic species as it was observed in previous works on the reduction of HCOOH where a black coating completely covered the surface of the copper [22, 23]. A second finding showing that deactivation does not occur is that the amount of all the products were in a linear relationship with the passed charge as it is expected by the Faraday's law (Fig.4).

3.3 The effect of the electrolysis medium.

In order to clarify which of the CO, CO_2 or HCOOH was the precursor of the obtained products some additional electrolysis experiments were performed at 70 ^0C (Table 2).As the concentration of H_3PO_4 decreases from 85% to 20% the concentration of CO in the outgoing gaseous stream decreased from 1330 to 320 ppm. In parallel, the %CE of CH_3OH was decreased from 27.6% to 10.5% and that of acetaldehyde from 25.8 to 11.8%. The decrease of the %CEs was balanced by an increase in the hydrogen %CE from 10 to 44%. This means that there is a relationship between the concentration of

CO and the %CEs of the main products. The %CE of the main products was not affected by further increase in the concentration of HCOOH from 1 to 10% w/v.

A comparison of the experiments performed in 85% H_3PO_4 solution containing 1% w/v HCOOH and in a CO saturated solution under the same conditions showed that the % CE of acetaldehyde was about the same (25% and 23% respectively) while the %CE of methanol was by 10.8% lower. The decreased % CE of CH_3OH was attributed to the fact that this experiment was performed in a closed system where the produced methanol was not stripped by the He stream resulting to an increased production of mono methyl phosphate. In a CO_2 saturated solution the %CEs of CH_3OH and CH_3CHO were significantly lower but in this experiment CO and formic acid having %CEs of 10.5 and 12% respectively were detected and this was expected since they are the main products of the reduction of CO_2. In this experiment we can also assume that CO was also the intermediate for the formation of the detected products. In a 0.1 M H_2SO_4 solution containing 1% HCOOH where decarbonylation of HCOOH was not observed, since CO was not detected in the gaseous stream, reduction products were not detected. This shows that the nature of the electrolyte plays a more important role than pH since the pH of a 0.1 M H_2SO_4 solution is about the same with that of a 85% H_3PO_4 solution. The conclusion which can be drawn from the above experiments is that the products formation is strongly related with the presence of carbon monoxide in the solution which suggests that CO is the key intermediate. In addition, the presence of CO in the solution is necessary for the formation of acetaldehyde and ethanol according to the pathway proposed by Hori et al [20]:

$$* CH_2 + CO \xrightarrow{2H^+ + 2e^-} CH_2 = CH_2OH \rightleftarrows CH_3CHO \xrightarrow{2H^+ + 2e^-} CH_3CH_2OH$$
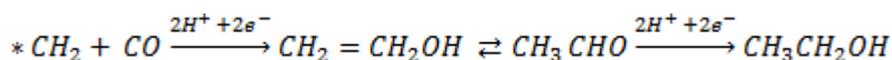
Ethanol which is one of the products detected at potentials more negative than -0.5 V is possibly produced from the electrochemical reduction of CH_3CHO by a consecutive reaction mechanism.

The presented results show that the reduction of HCOOH through its decarbonylation is an alternative way for its reduction because it leads to useful products such as CH_3OH and CH_3CHO at relatively high % CEs. The main disadvantage is that a part of the produced CH_3OH (about 25%) is converted to mono methyl phosphate and this makes difficult its separation.

4. Conclusion

This work shows that formic acid can be reduced through its decarbonylation route in concentrated 85% H_2PO_4 at 70 ^{0}C. The main products were CH_3OH and CH_3OH, while at more negative potentials CH_3CH_2OH was detected as a secondary of the reduction of CH_3CHO. The results showed that CO is the key intermediate for the formation of the detected products. The total %CE of the products decreased when the concentration of phosphoric acid was decreased, while it was not depended on the concentration of HCOOH. A part of the produced methanol (about 50%) reacted with H_3PO_4 and HCOOH to give the corresponding esters.

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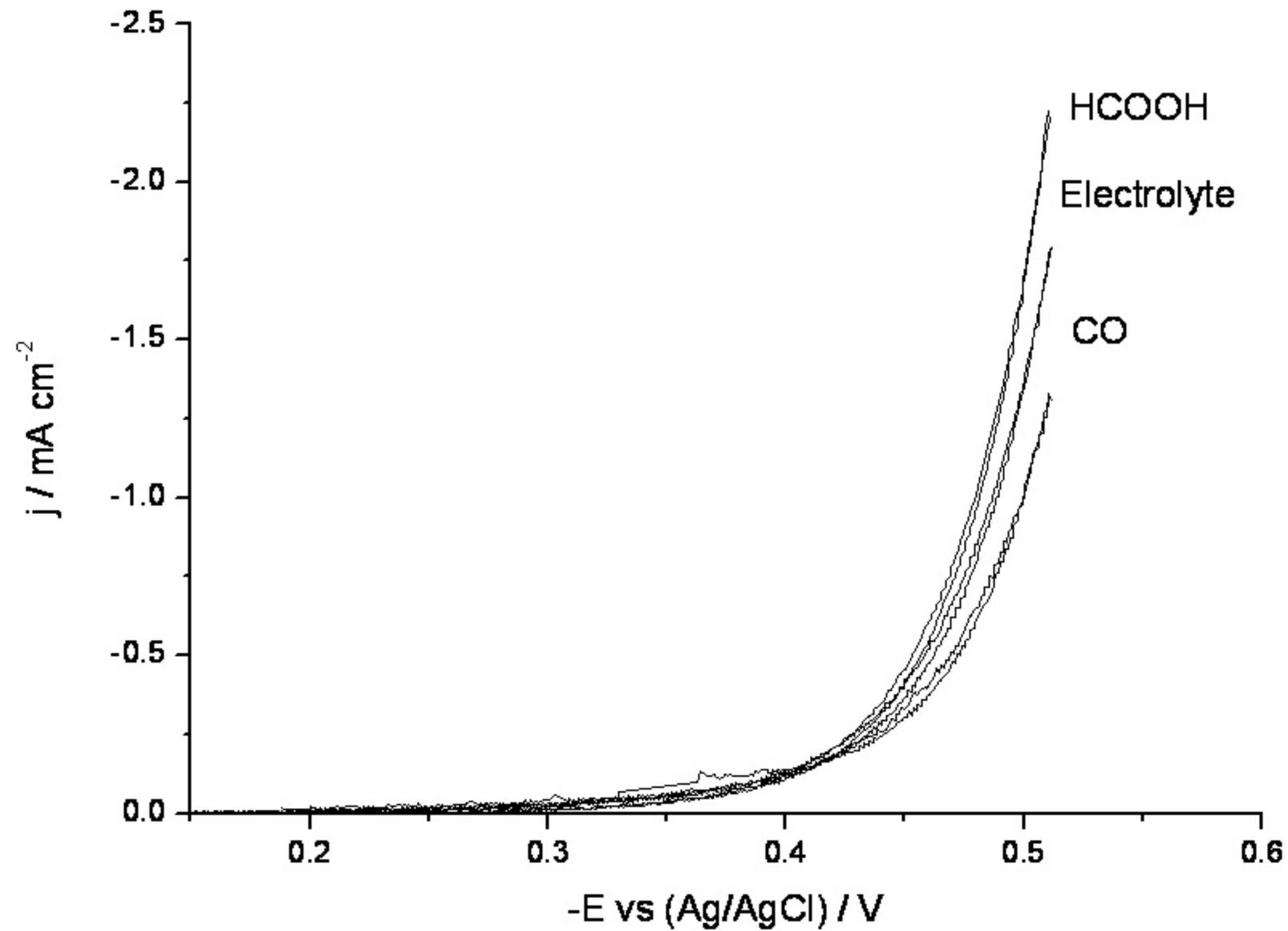
Figure 2. %CE of the products vs. potential in H_3PO_4 85% w/w containing 1% w/v HCOOH at $70\,^0$C ($\square$) CH_3OH, ($\blacktriangle$) CH_3CHO, ($\bullet$) CH_3CH_2OH, (∇) CH_4 and (o) C_2H_6
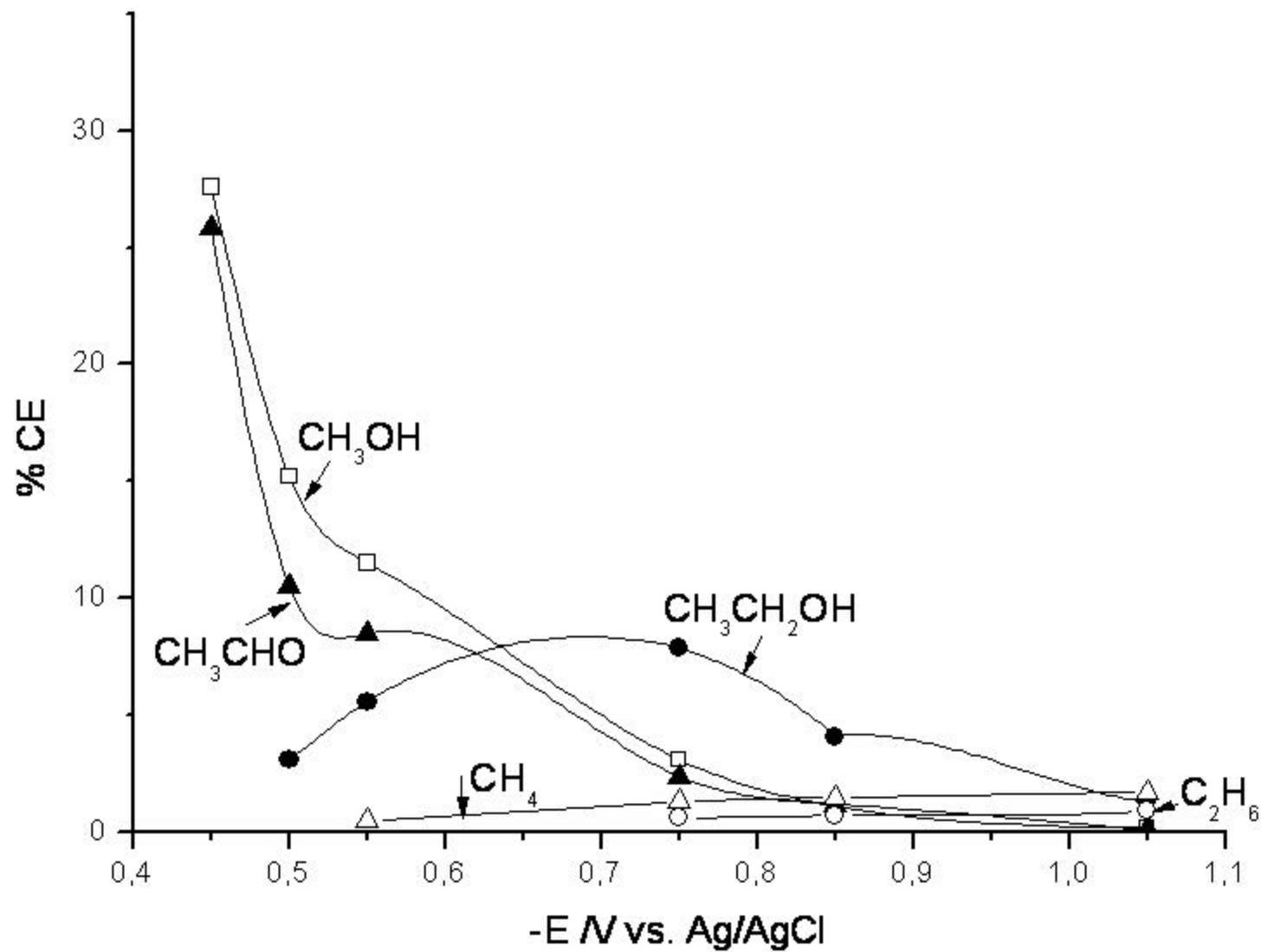
Figure 3. Electrolysis current density vs. time at various potentials in H_3PO_4 85% w/w containing 1% w/v HCOOH at $70\,^{0}C$
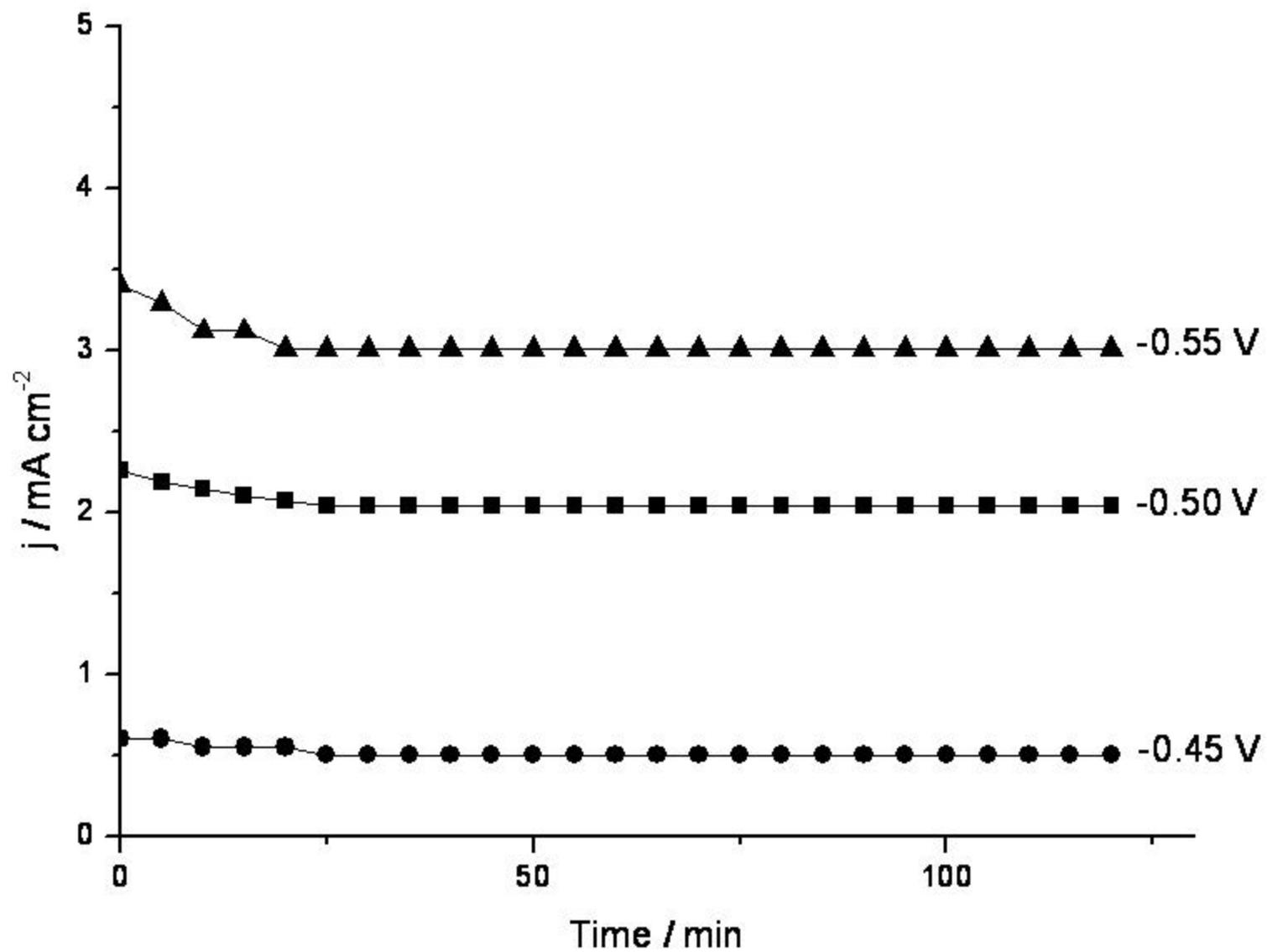
Figure 4. Mass of products vs. passed charge in H_3PO_4 85% w/w containing 1% w/v HCOOH at $70\,^0C$ and -0.55 V ($\square$) CH_3OH, ($\blacktriangle$) CH_3CHO, ($\bullet$) CH_3CH_2OH, (∇) CH_4 and (o) C_2H_6
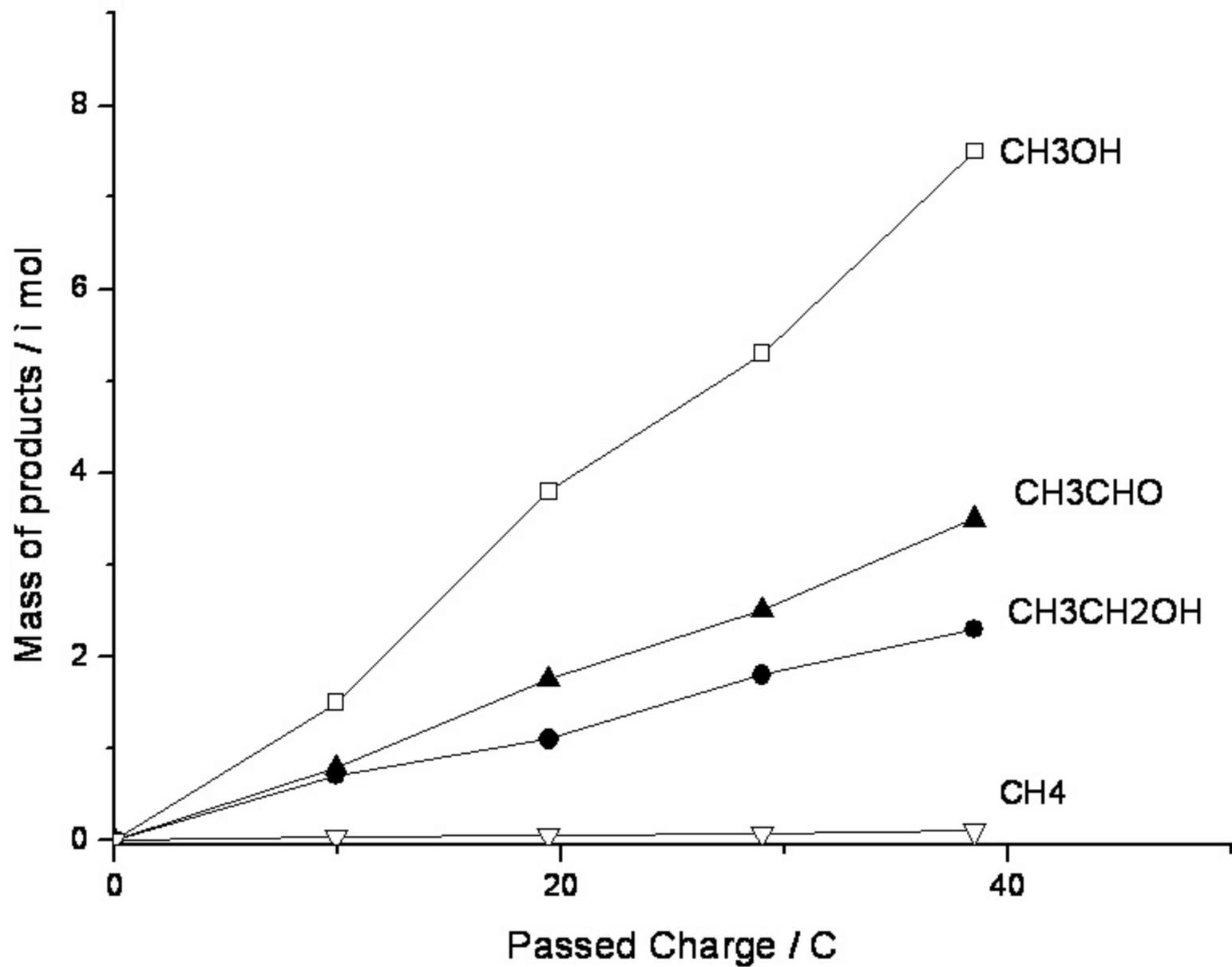
Table 1. %CEs of the reduction products at various potentials in 85% H_3PO_4 and 1% HCOOH at 70 ^{0}C

E/ V	%CE						Total CE	Total Charge /C
	CH_3OH	CH_3CH_2OH	CH_3CHO	CH_4	C_2H_6	H_2		
-0.45	27.6	-	25.8	-	-	10	63.4	6.48
-0.50	15.2	3.1	9.2	-	-	50	77.5	9.38
-0.55	11.5	5.6	7.5	0.5	-	62	87.1	21.14
-0.75	3.1	7.9	2.4	1.3	0.6	79	94.3	137.78
-0.85	1.1	4.1	1.2	1.5	0.7	89	97.6	321.44
-1.05	0.2	1.3	0.1	1.7	0.9	93	97.2	620.55

Table 2. The influence of the electrolyte on the %CEs of the products at 70 ^{0}C, at -0.45 V

Electrolyte	%CE					Total CE	Total Charge /C
	CH_3OH	CH_3CHO	CH_4	C_2H_6	H_2		
85% H_3PO_4 + 1%HCOOH	27.6	25.8	-	-	10	63.4	6.48
50% H_3PO_4 + 1%HCOOH	19.3	14.9	-	-	35	69.2	5.76
20% H_3PO_4 + 1%HCOOH	10.5	11.8	-	-	44	66.3	5.40
85% H_3PO_4 + 10%HCOOH	23.8	17.2	-	-	18	59.0	6.62
85% H_3PO_4 CO saturated	16.8	23.0	-	-	16	55.8	7.20
85% H_3PO_4 CO_2 saturated at -0.45 V	9.7	1.1	-	-	30	40.8*	5.76
0.1 M H_2SO_4+ 1% HCOOH	-	-	tr	-	98	98	6.2

*In this experiment HCOOH and CO were detected having %CEs of 10.5 and 12% respectively