

Literature Survey on Electrochemical Reduction of CO₂

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Abstract

The electrochemical reduction of carbon dioxide has been studied for a number of years and several good reviews have been written on the subject as well as papers investigating the reaction mechanisms for CO₂ reduction. Most of the focus has been investigating different products that can be formed using various catalysts with the majority of the work being done on metal electrodes in either aqueous or organic media. The main products of CO₂ reduction are methane, ethylene, formate (formic acid), carbon monoxide and some alcohols (methanol, ethanol, propanol). Since hydrogen evolution is a competing reaction, metals with high overpotential for hydrogen evolution, such as Hg, In, Pb, Cd, have higher efficiencies for CO₂ reduction. Because of their aprotic nature, organic electrolytes also help suppress hydrogen evolution in addition to having higher solubility of CO₂. Furthermore, several researchers have found that lower temperatures suppress hydrogen evolution and increase efficiency for CO₂ reduction. Copper has received a lot of attention because it produces appreciable amounts of hydrocarbons and alcohols from CO₂ reduction. There has also been some work on making alloy catalyst, most of which has been Cu alloys. However, copper and its alloys tend to give a mix of products, including hydrogen, rather than one product at high efficiency. At least a couple groups have also looked at the effect of the supporting electrolyte on the selectivity of CO₂ reduction at copper electrodes and have shown that it has a significant effect in both aqueous and organic media. Work has also been done to increase the reaction rate using gas diffusion electrodes (GDEs), and high CO₂ pressures, which has allowed current densities up to several hundred mA/cm² to be achieved.

Keywords: CO₂ Reduction, PVA solid polymer electrolyte, Ion exchange membrane.

1. Introduction

Current global environment problems are closely related to energy consumption problems. It is necessary to solve simultaneously both problems for continuous social-economical growth and for global environment protection. Establishment of fixation and recycling of CO₂ is one of the main problems of global environment protection. Energy-related activities, industrial processes, land use change and waste combustion are the main sources of the increase of carbon dioxide in the atmosphere causing environmental pollution and enhancement of the greenhouse effect. The large increase in emissions over the past couple of decades has resulted in the substantial accumulation of CO₂ in the atmosphere. This increase in percentage of CO₂ in atmosphere cause elevation in global temperature. These changes in climate could cause problems in many areas such as human health, agriculture, natural ecosystems, and coastal areas [1].

2. Literature Review

The main products are methanol, formic acid, formaldehyde, methane and syngas [2]. The different product formation is mainly depends on the selection of catalyst. As the major work have been done on metal catalyst. The selection of electrolyte is also very important parameter for electrochemical reduction of carbon dioxide [3]. Most of the work has been done by using aqueous electrolyte. Very few researchers used non aqueous electrolyte for the conversion of Carbondioxide. Many of researchers found that lower temperatures suppress hydrogen evolution and increase efficiency for CO₂ reduction. For getting higher faradaic efficiency the solubility of carbon dioxide should high High hydrogen overvoltage electrodes with negligible CO adsorption (such as Hg, Cd, Pb, Tl, In and Sn) can reduce CO₂ with a high current efficiency. Researchers showed interest in metal alloy also, they got good faradaic efficiency by using Copper metal alloys. However, Copper and its alloys tend to give a mix of products, including hydrogen. After using metal and metal alloy electrodes the researchers turns to gas diffusion electrodes which shows good current efficiency towards electrochemical reduction of Carbon dioxide.

2.1. Electrochemical reduction in aqueous medium

According to [4] the electrochemical reduction of CO₂ with a Cu electrode in methanol was studied for various potassium supporting salts. A review is provided in 2001 on the aqueous reduction of CO₂ to hydrocarbons at copper electrodes, covering the literature since the first report of the reaction in 1985 [5]. According to this review the reaction product distribution strongly depends on the conditions at which data has been reported. When used in the aqueous solution, most flat metallic electrodes yielded monoxide and formic acid [6]. Only copper was suitable electrode for the formation of hydrocarbons such as methane and ethylene, [7, 8]. Hori and his group carried out the

experiment and got faradaic efficiency for formic acid is about 90%. A maximum efficiency for methane formation was 27.0% in CH₃COOK/methanol catholyte at -3.0 V. By using Potassium halide [9] has got the result, that reduction of water to hydrogen is minimises. The mechanism for the electrochemical reduction of CO₂ in NaHCO₃ aqueous solution with a copper electrode was investigated [6]. When the electrolysis was conducted under nitrogen atmosphere, electrolysis yielded exclusively hydrogen. As formic acid and other hydrocarbon products some researchers got alcohols also product and only a few have reported high current efficiencies [10,11]. Cu alloys have also been investigated, but the main products obtained were CO, HCOOH and methanol, not hydrocarbons, and high selectivity could not be obtained [12]. [13] has shown that bulk PAn (Polyaniline) can be used as the cathode in the reduction of CO₂ with high current efficiencies and low overpotentials. Carbon monoxide is another product that has been produced with high efficiency by reducing CO₂ at various electrodes [2]. Instead of trying to suppress hydrogen evolution, another approach that has been used by some researchers is to control the relative rates of CO and H₂ production to make syngas of the correct composition [2]. The result of different product formation from different electrodes and electrolytes are summarized in table 1.

Table 1: Summary of literature results for the electrochemical reduction of CO₂.

Authors	Cathode	Electrolyte	Conditions			CD /mA·cm ²	Main products (faradaic efficiency /%)			
			T/K	P/Bar	pH		C ₂ H ₄	CH ₄	CO	HCOOH
Komastu et al. (1995)	Cu-Nafion	0.5 M K ₂ SO ₄	298	1	-	5	8.8	<0.1	0.6	5.9
	Cu-Nafion	0.5 M K ₂ SO ₄	298	1	-	5	3.5	<0.1	2.0	3.2
	Cu-selemion	0.5 M K ₂ SO ₄	298	1	-	5			10	15
Kaneco et al. (1999)	Cu-foil	CsOH in methanol	243	-	7.1	4	32.3	8.3	8.3	-
Kaneco et al. (2007)	Cu-foil	NaOH in methanol	243	-	5.3	12.9	17.6	63	-	-
Kaneco et al. (1999)	Cu-foil	CH ₃ COOK in CH ₃ OH	243	-	6.8	3.4	3.2	8.6	5.4	13.1
		KBr in CH ₃ OH	243	-	4.7	3.2	9.8	6.4	35	17.4
		KI in CH ₃ OH	243	-	4.6	4.72	19.9	15.1	15.2	-
Ikeda et al. (1987)	In	0.1 M TEAP/H ₂ O	-	-	-	-	-	-	6.8	87.6
Ikeda et al. (2008)	Cu-GDE (-325 mesh)	0.5 M K ₂ SO ₄	298	-	-	130	3.3	1.3	6.8	20.6
Hori et al. (1987)	Ag-AEM	0.2M K ₂ SO ₄	293	1	-	20	-	-	77.4	6.3
Udupa et al. (1971)	Hg/Cu	Na ₂ SO ₄ , NaHCO ₃	293	1	7-9	50	-	-	-	33
Li and Oloman (2005)	Sn/Cu (mesh)	KHCO ₃	300	0.2-1.2	7-8	178	-	-	-	36
Li and Oloman (2007)	Sn granuels	KHCO ₃ + KCl	293	6.9	7.5-8	60	-	-	-	91

[6] produced a roughly 1:1 ratio of hydrogen and carbon monoxide at a relatively low potential of -0.6V RHE. They estimated the energy efficiency for the cell

(producing oxygen at the anode) to be roughly 45%. They also demonstrated that the ratio of CO to H₂ can be controlled by the potential applied to the cell. The main products were CO and H₂ with the efficiencies ranging from 25%-50% and 40%-65% respectively [14]. Faradaic efficiencies for HCOOH and oxalic acid have been achieved in high pressure experiments at sp group metal electrodes with high overpotential for hydrogen evolution such as Pb [6], and Cu/Zn oxides [3]. Copper cathodes are among the most promising options for hydrocarbon manufacturing. [13] who achieved 90% efficiency for formic acid at a low potential of -1.1V vs. NHE and current density 80mA/cm².

2.2. Electrochemical reduction using solid polymer electrolyte

According to [14] an effective cathodic electrode was assembled with a porous PTFE sheet decorated with solid electrolyte and anion type solid polymer electrolyte. Current efficiency was reached up to 90 % for CO production on Au electrode. Work by Dewulf and Bard showed that the Cu/nafion electrode can be prepared by using a N₂H₄ reducing solution and a Cu (II) pyrophosphate plating solution, but it took a very long time approximately 2 weeks for electro reduction. Gas phase electrochemical reduction of CO₂ using Cu-SPE composite electrodes has been already investigated by [9]. [9] carried out the deposition of Cu on nafion membrane by the combination of CuSO₄ and NaBH₄, but the technique was not clearly described.

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