



# Article Techno-Economic Analysis of Electrocatalytic CO<sub>2</sub> Reduction into Methanol: A Comparative Study between Alkaline Flow Cell and Neutral Membrane Electrode Assembly

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Abstract: Electrocatalytic CO<sub>2</sub>-reduction technology can convert CO<sub>2</sub> into methanol and other chemicals using renewable electricity, but the techno-economic prospects of the large-scale electrocatalytic reduction in CO<sub>2</sub> into methanol are not clear. This paper conducted sensitivity analysis to confirm the key parameters affecting the cost of methanol production from an alkaline flow cell and a neutral MEA electrolyzer, compared the cost of the two electrolyzers under laboratory data and optimized data scenarios, and analyzed the key parameter requirements of the two electrocatalytic systems to achieve profitable methanol production. The results show that electricity price, Faradaic efficiency, cell voltage, and crossover/carbonate formation ratio are the most sensitive parameters affecting the cost of methanol production. The alkaline flow cell had higher energy efficiency than the MEA cell, but the saving cost of electricity and the eletrolyzer cannot cover the cost of the regeneration of the electrolyte and CO<sub>2</sub> lost to carbonate/bicarbonate, resulting in higher methanol production costs than the MEA cell. When the crossover/carbonate formation ratio is zero, the cost of methanol production in an alkaline flow cell and a neutral MEA cell can reach under 400 USD/tonne in the cases of energy efficiency more than 70% and 50%, respectively. Therefore, enhancing energy efficiency and ensuring a low crossover/carbonate formation ratio is important for improving the economy of electrocatalytic methanol production from CO<sub>2</sub> reduction. Finally, suggestions on the development of electrocatalytic CO<sub>2</sub> reduction into methanol in the future were proposed.

Keywords: electrocatalysis; CO2 reduction; technical economy; electrolyzer

## 1. Introduction

The intensive use of fossil fuels has caused a large amount of  $CO_2$  emissions, resulting in a series of environmental problems, such as global climate change. Carbon capture, utilization, and storage technology (CCUS) represents key technology to achieve a reduction in carbon emissions from fossil energy sources [1]. Converting and utilizing  $CO_2$ from industrial emission sources can reduce the cost of CCUS technology while providing high-value-added fuels or chemicals. With the development of renewable-energy-powergeneration technologies, such as photovoltaic power and wind power, electrocatalytic  $CO_2$ -reduction technology can use renewable electricity to reduce and convert  $CO_2$  into valueadded fuels or chemicals, such as carbon monoxide and methanol, under mild conditions, reducing  $CO_2$  emissions and storing electrochemical energy, which has many potential applications [2–6].

Methanol has many advantageous properties, including high energy density and convenient transportation and storage [7]. It is an important platform molecule and a clean fuel. Traditional coal-to-methanol technology produces high carbon emissions, and



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). electrocatalytic  $CO_2$ -reduction technology is expected to provide a new method of lowcarbon methanol production. Previous studies have reported on the techno-economic analysis of electrocatalytic methanol production from  $CO_2$  and predicted its prospects for commercial applications [8–11]. Jiao et al. [8] used net present value as an evaluative indicator and analyzed the economic feasibility of the process of electro reducing  $CO_2$ to methanol. Na et al. [12] analyzed the profit potential of the electro reduction in  $CO_2$ to methanol when coupled with different oxidation reactions, such as oxygen evolution reactions, organic oxidation reactions, etc. However, the above studies only used simple models of the electrocatalytic process without considering the impact of differences in electrolyzer type, electrolytes, or the related separation and recovery processes on the economy of methanol production. The evaluation model still needs to be further improved.

Alkaline flow cells and neutral membrane electrode assembly (MEA) are widely used as CO<sub>2</sub> electrolyzers in the literature [13–15]. They have the advantages of compact structure, high current density, low cell voltage, etc. [16,17]. This is especially true for the stackable neutral MEA electrolyzer, which is more suitable for industrial applications of CO<sub>2</sub> catalysis. However, carbonate formation and crossover in alkaline flow cells and neutral MEA electrolyzers cause a lot of CO<sub>2</sub> loss [18,19], resulting in increased cost of electrolyte regeneration and CO<sub>2</sub> recovery, and the current economic model for the electrocatalytic reduction in CO<sub>2</sub> to methanol does not consider this issue. Therefore, it is necessary to systematically analyze the economics of the electrocatalytic reduction in CO<sub>2</sub> to methanol in different electrolyzers and to determine the most effective path to cost reduction.

This paper constructs a techno-economic model of the electrocatalytic reduction in  $CO_2$  to methanol in alkaline flow cells and neutral MEA electrolyzers and identifies and explores the influence of the main parameters of the process on production cost. The cost composition of electrocatalytic methanol production in two electrolyzers under different situations is compared and analyzed, and the main ways to reduce the cost of methanol production are determined. Finally, by comprehensively analyzing the influence of carbonate formation/crossover and energy efficiency on methanol cost, the key parameter values that can bring methanol production close to profitable are determined.

## 2. Model for CO<sub>2</sub> Electrolyzer System

Alkaline flow cells and neutral MEAs are two typical CO<sub>2</sub>-reduction electrolyzers used in the literature [20,21]. In this paper, we developed economic models of these two electrolyzer systems that calculated the material and energy balances involved in the processes and estimated the required capital investment and operating costs. This yielded a comparison between the cost of CH<sub>3</sub>OH production by different electrolyzers and the sensitivity of CH<sub>3</sub>OH production costs and changes in operating parameters.

 $CO_2$  feedback can come from point sources, such as a power plant with a  $CO_2$  capture unit, or air, by using direct air capture (DAC) technology. For an alkaline-flow-cell electrolyzer (Figure 1A), it consists of three flow channels: one is for  $CO_2$  flow, while the other two are for catholyte and anolyte flow.  $CO_2$  is fed into the cathode compartment of the electrolyzer and flows through the GDLs to reach the catalyst/catholyte interface for the  $CO_2$ -reduction reaction. The gaseous-reduction products and unreacted  $CO_2$  stream outflow the cathode chamber, and the unreacted  $CO_2$  is separated by a pressure swing adsorption (PSA) unit and recycled into the cathode compartment. The methanol generated from  $CO_2$  reduction dissolves in the catholyte and is separated from the electrolyte by a distillation process [8]. During electrocatalytic  $CO_2$  reduction, some of the  $CO_2$  in the cathode compartment passes through the gas diffusion layer and dissolves in the catholyte (7 mol/L KOH solution) to form K<sub>2</sub>CO<sub>3</sub>, which may form K<sub>2</sub>CO<sub>3</sub>/KHCO<sub>3</sub> precipitation and block the cathode due to the low solubility of  $K_2CO_3$ . The  $CO_2$  lost to  $K_2CO_3$  is recovered by a calcium-alkali recovery-cycle system and then enters the cathode chamber of the electrolyzer. In the anode compartment, the water in the anolyte  $(0.1 \text{ mol/L KHCO}_3)$ is oxidized by the anode to produce oxygen.



Cathodic reactions:  $CO_2+6e^-+6H^+\rightarrow CH_3OH+H_2O$ ;  $2H^++2e^-\rightarrow H_2$ Anodic reactions:  $2H_2O-4e^-\rightarrow O_2+4H^+$ 

Carbonate formation reaction in catholyte:  $CO_2+2KOH \rightarrow K_2CO_3+H_2O$ ;  $CO_2+KOH \rightarrow KHCO_3/KHCO_3$ Cathode catalyst: Cu-based catalyst

Anode catalyst: IrO<sub>2</sub>

Membrane: anion exchange membrane(AEM)



**Figure 1.** (**A**) Process flow diagram of methanol production via alkaline flow cell. (**B**) Process flow diagram of methanol production via neutral MEA electrolytic cell.

MEA electrolyzer consists of a cathode and anode, which are separated by an ionexchange membrane). The side of the cathode loading catalyst is directly pressed against the ion-exchange membrane in a zero-gap configuration. A key difference between an MEA and alkaline-flow-cell electrolyzer is that humidity must be fed to keep the membrane hydrated during operation. The MEA electrolyzer has no catholyte, which avoids possible electrolyte flooding, the recovery of  $CO_2$  from bicarbonate/carbonate salts, and the regeneration of catholyte.

In detail, for a neutral MEA electrolyzer (Figure 1B), a  $CO_2$  and water-vapor mixture enters the cathode chamber of the electrolyzer and is reduced on the cathode. The outlet gas of the cathode chamber includes the reduction products, including methanol, H<sub>2</sub>, and unreacted water vapor/ $CO_2$ . After passing through the cold trap, methanol and water vapor are separated from the mixture to form a methanol solution, which is then distilled to obtain methanol. The remaining unreacted  $CO_2$  gas is recycled into the cathode chamber of the electrolyzer after PSA separation. The water in the anolyte (0.1 mol/L KHCO<sub>3</sub>) is oxidized by the anode to produce oxygen. During the reaction process, some of the  $CO_2$  passes through the ion-exchange membrane, entering the anode chamber and mixing with the oxygen produced by the anode, which is called  $CO_2$  crossover. The lost  $CO_2$  is then separated by a carbon-capture device and recycled into the cathode chamber for  $CO_2$ -reduction reaction.

For the above two reaction systems, it is assumed that  $H_2$  is the only cathode byproduct and that methanol will not penetrate the ion-exchange membrane from the cathode chamber into the anode chamber. For this reason, we only consider the crossover of CO<sub>2</sub> in MEA and CO<sub>2</sub> dissolving in the catholyte KOH (7 mol/L) to form K<sub>2</sub>CO<sub>3</sub>/KHCO<sub>3</sub> in the alkaline flow cell. The concentration of CH<sub>3</sub>OH in the products is assumed to be 95 wt.% after distillation separation, which is modeled as a single-column system.

The techno-economic evaluation models in this paper follow the general principles of previous existing models. On this basis, a special sub-cost analysis is carried out for the different electrolyzer types. In order to better compare the two electrolyzers, the models in this paper make assumptions about certain processes and parameters. It is assumed that the annual methanol production is 35,000 tonnes/year and that the electrolyzer life is 20 years. The electrolyzer capital cost was obtained by calculating the amount of electrolyzer materials required for the electrolyzer body structure, membrane, electrolyte, and catalyst, considering their corresponding lifetime. The electrolyzer operation cost includes electricity cost, input chemical cost (CO<sub>2</sub>, water, electrolyte), and other operating costs, including repairing and labor costs. In addition, the capital and operation costs of the external unit for recovering the lost CO<sub>2</sub>, including cathode separation, anode separation, and catholyte regeneration, are also considered. Cathode separation includes methanol distillation and separation of  $CO_2$  and hydrogen from the cathode outlet gas stream by a PSA system. Anode separation is the separation of  $CO_2$  and  $O_2$  from the anode outlet gas stream of the MEA electrolyzer by a carbon-capture system. Catholyte regeneration means, in the alkaline flow cell, the recovery of CO<sub>2</sub> dissolved in KOH by the thermal calcium-alkali recovery cycle. The detailed cost calculation method is shown in the supporting information. Table S1 shows the invariable inputs data for neutral MEA cell and alkaline flow cell.

## 3. Economic Cost Analysis

#### 3.1. Sensitivity Analysis

Before comparing the economy of the two different electrocatalytic systems, we first conducted sensitivity analysis of their methanol production costs to determine the main parameters that affect the final methanol cost. Figure 2 shows the results of the sensitivity analysis of methanol production cost for two flow cells when the crossover/carbonate formation ratio = 0, that is, the methanol cost changes with different parameters. The parameter values at the center point (x = 100%) are as follows: electricity price (0.02 USD/kWh); current density (300 mA/cm<sup>2</sup>); cell voltage (2.5 V); single-pass conversion (50%); Faradaic efficiency (50%); and system lifetime (20 years). The steeper the slope of the curve, the more sensitive methanol cost is to the corresponding parameter.

As shown in Figure 2A, for the alkaline flow cell, the cost of methanol gradually decreased with the increase in Faradaic efficiency, system lifetime, current density, and single-pass conversion, while it increased with the increase in cell voltage and electricity price. Among them, the most sensitive parameters are electricity price and Faradaic efficiency, followed by system lifetime and cell voltage. As shown in the Supplementary Materials, the increase in electricity price raises the costs of electricity, PSA operation, carbonate regeneration operation, and other operations, such as repairing and labor. The increase in Faradaic efficiency decreases the capital costs of the electrolyzer, catalyst, membrane, electrolyte, and the costs of electricity and other operations, as well as the costs of PSA separation operation, BoP, and installation.

Single-pass conversion ratio [22] (defined as reduced  $CO_2/(unreacted CO_2 at cathode outlet + reduced CO_2))$  has almost no effect on methanol cost when greater than 20%. In our model, single-pass conversion mainly changes the cost of cathode separation in the

alkaline flow cell. Higher single-pass conversion leads to a lower cost of cathode separation. When the single-pass conversion is larger than 20%, its change has little effect on the cost of cathode separation. Low single-pass conversion is possible because in our model, the cost of recovering unreacted  $CO_2$  from the cathode outlet gas stream is lower than the cost of purchasing new  $CO_2$ . If the cost of former is higher, from the aspect of economy, it is preferred to buy new  $CO_2$  rather than to recover unreacted  $CO_2$ . Furthermore, in this situation, high single-pass conversion may be more important.



**Figure 2.** Sensitivity analysis of the cost of methanol production in an alkaline flow cell (**A**) and a neutral MEA electrolytic cell (**B**); (**C**) the impact of crossover/carbonate formation ratio on the cost of methanol production in an alkaline flow cell and a neutral MEA electrolysis cell.

The current density curve is relatively flat near 150% (450 mA/cm<sup>2</sup>) but steeper around 50% (150 mA/cm<sup>2</sup>); this indicates that when the current density is greater than 300~500 mA/cm<sup>2</sup>, its impact on methanol cost is not significant, and a large current density has little impact on reducing cost. In our model, current density mainly affects the capital cost of the electrolyzer, electrolyte, catalyst, and membrane. The higher current density is, the lower capital cost. When the current density is large enough, the capital cost only accounts for a small proportion of the total cost. Therefore, the reduction in methanol cost is not obvious when further raising the current density. When the current density is at a high level, reducing cell voltage and increasing Faradaic efficiency, system lifetime, and other parameters are priority strategies for reducing methanol cost. Reducing electricity price is the most critical and effective external measure for improving the economy of alkaline-flow-cell electrocatalytic methanol production.

As shown in Figure 2B, similar to the alkaline flow cell, the cost of methanol production in a neutral MEA electrolyzer is also positively correlated with cell voltage and electricity price, while it is negatively correlated with Faradaic efficiency, system lifetime, current density, and single-pass conversion. The cost of methanol production by the neutral MEA electrolyzer is most sensitive to cell voltage, electricity price, and Faradaic efficiency. As with the alkaline flow cell, the methanol cost of the neutral MEA electrolyzer is not significantly affected by the change in current density after the current density exceeds 100% (300 mA/cm<sup>2</sup>). Similarly, the single-pass conversion rate has little effect on methanol cost after it exceeds 20%. Unlike with the alkaline flow cell, a change in the system lifetime has no obvious impact on the methanol production cost of the MEA electrolyzer after it exceeds 100% (20 years). This may be because, in our model, the lifetime of the system affected the capital cost of the eletrolyzer system. We introduced a capital recovery factor (CRF) to turn the one-time capital cost of the eletrolyzer into a daily cost, which can be calculated as follows:  $CRF = i(1 + i)^{lifetime} / [(1 + i)^{lifetime} - 1]$ . Additionally, the capital cost of the eletrolyzer is proportional to CRF, therefore, based on the equation, the decreasing trend in capital cost gradually slows down with the increase in lifetime. The MEA has no catholyte and low methanol distillation costs. Figure 2C shows the relationship between methanol production cost and crossover/carbonate formation ratios of the two electrolyzers. It can be seen that the change in crossover/carbonate formation ratios has a significant impact on methanol cost. A higher crossover and carbonate formation rate lead to a significant increase in  $CO_2$  recovery cost for the whole system. In addition, when the parameters of both electrolyzers are exactly the same, the methanol production cost is significantly higher for the alkaline electrolyzer than for the MEA. The reasons for this will be explored through the sub-cost analysis.

Cell voltage is another important factor affecting methanol cost. The alkaline flow cell has the advantages of low cell voltage and high energy efficiency [20], but its electrocatalytic chemical production cost is limited by carbonate formation. The MEA electrolyzer can largely avoid carbonate formation, but its cell voltage is usually high [23]. In order to clarify the sensitivity of methanol cost to cell voltage and crossover/carbonate formation, we analyzed the impact of changes in cell voltage and crossover/carbonate formation on methanol cost, respectively. As shown in Figure 3, reducing crossover/carbonate formation is more effective than reducing cell voltage at reducing methanol cost for both the alkaline flow cell and the MEA electrolyzer. Therefore, although it would increase cell voltage, optimizing the electrode/electrolyzer design by using a bipolar membrane would reduce carbonate formation [24] and therefore reduce methanol cost. However, this phenomenon is not particularly significant for the MEA electrolyzer (Figure 3B). This is because, after reducing carbonate formation, the cost of catholyte regeneration and  $CO_2$  recovery in the alkaline-flow-cell system is significantly reduced. While reducing crossover in the MEA electrolyzer reduces the cost of anode  $CO_2/O_2$  separation, this part of the cost accounts for a relatively low proportion. Therefore, in order to achieve low-cost methanol production, it is very important to reduce crossover/carbonate formation and cell voltage at the same time.



**Figure 3.** (A) The influence of carbonate formation rate and cell voltage on the production cost of methanol in an alkaline flow cell. (B) The influence of  $CO_2$  crossover and cell voltage on the cost of methanol production in an MEA electrolytic cell.

## 3.2. Comparative Analysis of the Cost of Methanol Production between Two Types of Cells

Next, we compare the cost of electrocatalytic CO<sub>2</sub> methanol production by the alkaline flow cell and MEA electrolyzer systems. Costs are based on reported and optimized data, with the assumption that the electricity price is 0.02 USD/kWh. For the MEA electrolyzer, we consider the cost of recovering  $CO_2$  due to crossover. For the alkaline flow cell, we calculated the cost of regenerating and recovering  $CO_2$  from the catholyte. So far, most of the research on CO<sub>2</sub> electrocatalytic reduction into methanol has been carried out in H-type reactors [25–27], with only a few studies using an MEA electrolyzer or alkaline flow cell [28]. Peter et al. reported [29] that in an alkaline flow cell, when the catholyte was 1 mol/L KOH solution, the CuGa intermetallics achieved 76% Faraday efficiency of methanol production at -0.3 V vs. RHE potential. Kong et al. [28] reported 70% Faraday efficiency of methanol production in a 5 cm<sup>2</sup> MEA electrolyzer at a full cell voltage of 3.4 eV. To model the impact of crossover/carbonate formation on cost, we set the MEA electrolyzer crossover ratio and alkaline-flow-cell carbonate formation at 4 and 24, respectively, and the single-pass conversion rate was set at 30%, according to data reported in the literature [22]. These data indicators constitute the laboratory data input in this work. In order to predict future methanol costs, we determined the cost input under the optimized situation by combining data from a water electrolyzer and a CO<sub>2</sub> electrolyzer with optimized situation data reported by many previous studies [17,30–35].

By calculating the composition of methanol cost for the two electrolyzers under laboratory and optimized conditions, we can evaluate the economy of electrolyzers and analyze the main ways to reduce the cost of methanol production. Table 1 gives the detailed input data of the two electrolyzers under laboratory and optimized conditions. The Supporting Information provides the calculation method and the equation of the cost of methanol in the alkaline flow cell and the neutral MEA cell. Figure 4 gives the cost composition of electrocatalytic methanol production by two electrolyzers under different conditions. Because the market price of methanol is fluctuating, we chose 400 USD/tonne as the reference price.

Table 1. Data input for two types of electrolyzers under laboratory and optimized scenarios.

er	Cell Voltage (V)	Faradaic Efficiency (%)	Current Density (mA/cm <sup>2</sup> )	Electrical Energy Efficiency (%)	Crossover/Carbonate Formation Ratio	Single-Pass Conversion (9

Cell Voltage (V)	Faradaic Efficiency (%)	(mA/cm <sup>2</sup> )	Electrical Energy Efficiency (%)	Formation Ratio	Single-Pass Conversion (%)	
3.4	70	100	24.7%	4	30	
2.5	78	200	37.0%	24	30	
2.0	90	1000	54.0%	2	40	
2.0	90	1000	54.0%	12	40	
	Cell Voltage (V) 3.4 2.5 2.0 2.0	Cell Voltage (V) Faradaic Efficiency (%)   3.4 70   2.5 78   2.0 90   2.0 90	Cell Voltage (V) Faradaic Efficiency (%) Current Density (mA/cm²)   3.4 70 100   2.5 78 200   2.0 90 1000   2.0 90 1000	Cell Voltage (V) Faradaic Efficiency (%) Current Density (mA/cm²) Electrical Energy Efficiency (%)   3.4 70 100 24.7%   2.5 78 200 37.0%   2.0 90 1000 54.0%   2.0 90 1000 54.0%	Cell Voltage (V)Faradaic Efficiency (%)Current Density (mA/cm²)Electrical Energy Efficiency (%)Crossover/Carbonate Formation Ratio3.47010024.7%42.57820037.0%242.090100054.0%22.090100054.0%12	Cell Voltage (V)Faradaic Efficiency (%)Current Density (mA/cm²)Electrical Energy Efficiency (%)Crossover/Carbonate Formation RatioSingle-Pass Conversion (%)3.47010024.7%4302.57820037.0%24302.090100054.0%2402.090100054.0%1240



Figure 4. Cost composition of methanol production for two electrocatalytic systems.

It is obvious that, for the alkaline flow cell, the cost of catholyte regeneration dominates, accounting for more than 60% of methanol production costs in both the laboratory and

in the optimized situation. Next is the cost of electricity. Compared to the operation cost, the total capital cost, including materials for the electrolyzer body structure, membrane, electrolyte and catalyst, cathode separation, and anode separation, is much lower (equal to the cost of installation), which means that reducing electrolyte regeneration cost is much more important in reducing methanol production cost in the alkaline flow cell. Although the carbonate ratio decreased from 24 to 12 under the optimized situation, the cost of catholyte regeneration was still high, which means the cost of the alkaline flow cell is much higher than the reference price of methanol. Actually, if the carbonate formation ratio is zero, the cost of methanol production of the alkaline flow cell under the optimized situation is very close to the reference price of methanol.

For the MEA electrolyzer, there is no catholyte and no cost of recovery of  $CO_2$  lost in KOH and the regeneration of the catholyte. When using the laboratory data, the capital cost of the electrolyzer (including electrolyzer body structure, membrane, electrolyte and catalyst), installation cost, and electricity costs account for a high proportion of the total because of the lack of cost for catholyte regeneration. In addition, the cost of electricity, capital, and installation of the neutral MEA cell is higher than that of the alkaline flow cell, which is due to the fact that the MEA cell usually has a larger cell voltage and smaller Faradaic efficiency. Nevertheless, the cost of methanol production in the MEA cell is lower than that in the alkaline flow cell because the catholyte regeneration cost is too high due to the large carbonate formation rate. Therefore, reducing the carbonate formation rate and reducing catholyte regeneration costs are very important and effective for improving the economy of the alkaline flow cell when using either laboratory data or optimized situation data.

Comparing the cost of the neutral MEA cell under laboratory and optimized situations, it is found that with the increase in the energy efficiency (proportional to the Faradaic efficiency/cell voltage) of the neutral MEA electrolyzer, the capital, installation, and electricity operation costs are significantly reduced. Under the optimized situation, the methanol production cost of the MEA electrolyzer is very close to the reference cost. Further improving energy efficiency and reducing crossover can make the cost of methanol production from the MEA electrolyzer competitive on the market, which means that it is important to obtain a rational design of the catalyst/electrode, membrane, electrolyte, etc., to achieve high energy efficiency and low crossover.

We aim to further figure out the parameter values that enable the two electrocatalytic systems to achieve profitable methanol production with a significantly reduced crossover/carbonate formation ratio. As shown in Figure 5, considering that energy efficiency is a function of cell voltage and Faraday efficiency, we analyze the impact of energy efficiency and the crossover/carbonate formation ratio on methanol production cost. Other optimized parameters were also used.





For the alkaline flow cell (Figure 5A), methanol production cost reaches under 400 USD/tonne only when the energy efficiency is above 70%. When the carbonate formation ratio is larger than 0.25, the methanol production cost cannot reach the reference price, even if energy efficiency exceeds 90%. This is because the cost of carbonate regeneration is very high if the carbonate formation ratio is large. For the MEA electrolyzer (Figure 5B), when the crossover/carbonate formation ratio is zero and energy efficiency reaches 50%, methanol production cost can be lower than 400 USD/tonne. When the crossover/carbonate formation ratio is 2 and energy efficiency reaches 70%, methanol production cost can also reach the reference price. When the crossover/carbonate formation ratio increases further, the energy efficiency required to reach the methanol reference price is very high and difficult to achieve.

Compared with the alkaline flow cell, the elimination of the catholyte in the MEA cell removes the possibility of flooding of the gas diffusion electrode, electrolyte impurity deposition onto the catalysts, and the generation of bicarbonate/carbonate salts, thereby removing multiple sources of instability and saving the cost of regeneration of the catholyte. As a result, the MEA electrolyzer requires lower electronic energy efficiency to achieve low-cost methanol production. Therefore, for both the alkaline flow cell and the MEA electrolyzer, reducing the crossover/carbonate formation ratio is very important for reducing methanol production costs.

Considering the features of the alkaline flow cell and the neutral MEA cell, tandem electrocatalytic CO<sub>2</sub> reduction may be a promising way of combining the advantages of the two kinds of electrolyzers. The CO<sub>2</sub> electrocatalytic reduction process can be performed in two consecutive steps: CO<sub>2</sub> reduction into CO, followed by CO reduction into target CO<sub>2</sub>-reduction products. The CO<sub>2</sub> to CO process can be conducted in the neutral MEA cell to avoid the formation of carbonate. Furthermore, the CO-reduction reaction can be conducted in the alkaline flow cell. Due to the low solubility of CO in water/KOH, carbonate formation can also be suppressed in the case of CO reduction through tandem CO<sub>2</sub> to CO in the MEA cell and CO to products in the alkaline flow cell. Actually, some of the literature has reported enhanced two-step tandem CO<sub>2</sub> electrocatalytic reduction into  $C_{2+}$  products [36]. Many papers reported CO<sub>2</sub> conversion to CO in the MEA cell [17,37,38], while very few papers focused on electrocatalytic reduction in CO into methanol, requiring further investigation.

## 4. Conclusions

This study carried out a sensitivity analysis on the cost of methanol production from an alkaline flow cell and a neutral MEA electrolyzer. The results show that the cell voltage, electricity price, Faraday efficiency, cell voltage, and crossover/carbonate formation ratio are the most sensitive parameters affecting cost. Furthermore, comparing the cost composition of the two electrolyzers under laboratory data and optimized data scenarios, it was found that the methanol production cost of the neutral MEA electrolyzer was lower than that of the alkaline flow cell. Although the alkaline flow cell has a higher energy efficiency and lower electricity, capital, and installation costs, the catholyte regeneration and  $CO_2$ recovery cost account for too high a proportion (60%) due to the high carbonate formation ratio, resulting in a higher total methanol production cost than that of the MEA electrolyzer. Improving energy efficiency and reducing crossover/carbonate formation is an effective route to reducing the cost of methanol production. Then, the requirements for the key parameters of the two electrocatalytic systems to achieve profitable methanol production were analyzed. The results show that when the crossover/carbonate formation ratio is zero, the cost of methanol production in an alkaline flow cell can reach under 400 USD/tonne when the energy efficiency is >70%. When the energy efficiency of the neutral MEA reaches 50%, the methanol production cost can be lower than 400 USD/tonne. MEA electrolyzers are therefore more likely to be applied in the near future. When the crossover/carbonate

formation ratio is high, the energy efficiency required by both electrolyzers increases rapidly and is difficult to achieve.

Therefore, developing advanced catalysts/electrode/membrane components with low cell voltage and high faradaic efficiency, as well as designing a novel electrolyte system to suppress crossover/carbonate formation, should be is important for improving the economy of electrocatalytic methanol production. In addition, tandem electrocatalytic CO<sub>2</sub> reduction that conducts CO<sub>2</sub> reduction in two consecutive steps, i.e., CO<sub>2</sub> to CO and then CO to target CO<sub>2</sub>-reduction products, may also be a promising way to enhance the economy by combining the advantages of single electrolyzers.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/catal13061005/s1, Table S1: Invariable inputs data for neutral MEA cell and alkaline flow cell. References [39–47] are cited in the Supplementary Materials.

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