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Electrochemical Synthesis of Dimethyl Carbonate from CO₂ and Methanol over

Carbonaceous Materials Supported DBU in a Capacitor-like Cell Reactor

Yingjie Zhou[a,b,§], Zhongwei Fu[a,§], Shuanjin Wang[a], Min Xiao[a]*, Dongmei Han[a], Yuezhong

Meng[a]*

[a] The Key Laboratory of Low-carbon Chemistry & Energy Conservation of Guangdong

Province / State Key Laboratory of Optoelectronic Materials and Technologies, Sun Yat-sen

University, Guangzhou 510275, PR China

[b] School of Physics and Optoelectronic Engineering, Nanjing University of Information

Science & Technology, 219 Ningliu Road, Nanjing, Jiangsu 210044, China

*Corresponding authors: Tel.：+86 2084115506，Fax：+86 2084114113

[§] Who contribute equally to this work.

E-mail address: mengyzh@mail.sysu.edu.cn (Yuezhong Meng) or stsxm@mail.sysu.edu.cn

(Min Xiao)

ABSTRACT:

The electro-assisted dimethyl carbonate (DMC) formation from CO_2 and methanol over carbonaceous materials supported 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) were first performed under solvent-free conditions in a capacitor-like cell reactor designed by our group. The effects of applied voltage modes and conductivities of catalysts on the catalytic performances were fully investigated. The experiment results demonstrated that the catalytic activities can be obviously boosted when the voltages were applied to the catalyst fixed-bed. The constant working potential presented better catalytic activity than the metabolic voltages, and the higher conductivity of catalysts leads to a better catalytic performance. Furthermore, the supported DBU displayed good recyclable properties in the special designed electrochemical apparatus. We proposed the reaction mechanism of the electrocatalysis for DMC formation.

Key Words: Dimethyl carbonate, Carbon dioxide, Electrocatalysis, DBU

1. Introduction

The emissions of CO_2 have been dramatically increased within the past years and are still increasing each year. CO_2 emissions are considered as the major cause of global warming.[1] Recently, the usage of CO_2 has drawn many scientists' attention for it is recognized as a naturally abundant, nontoxic and recyclable carbon source for the production of fuels and chemical feedstock.[2-4]

Dimethyl carbonate (DMC) has gained increasing interest because of its benign nature and wide applications. It is used as an alternative methylating and carbonylating reagent to the notorious phosgene and dimethyl sulfate in many organic synthesis.[5] It is also used as an octane booster in gasoline due its high oxygen content[6] and electrolyte of lithium-ion batteries for facilitating the flow of free electrons.[7] Several routes have been developed for the DMC synthesis:[8] methanolysis of phosegene; oxidative carbonylation of methanol; methylnitrite carbonylation processes; transesterication of alkene carbonate or urea with methanol and the direct DMC formation from CO_2 and methanol. However, the former four synthesis methods involve using toxic, explosive and corrosive gases such as phosgene, nitric oxide or carbon monoxide. Hence, the direct DMC formation from CO_2 and methanol is one of the promising route from the views of green chemistry and sustainable development.[2] The big challenge of converting CO_2 and methanol into DMC is not only to activate the highly stable CO_2 molecule but also to shift the reaction to the right because of the thermodynamic restrictions.[9] A number of approaches in improving the DMC yield have been developed,[10] which include adding coreagents [11] in the reaction systems, carrying out the reaction in supercritical CO_2,[12] removing water by dehydrating agent [13] and developing efficient catalysts.[14] However, the DMC yield is

far away from satisfaction. Although all of these methods are still pursued today, some new technologies, such as the introduction of photocatalysis,[15] electrocatalysis,[16] and the development of membrane reactors, [17]have been tried to improve the DMC yields . Among them, the electrochemical fixation of CO_2 is considered to be a much effective route than these historical processes.[18-20] The electrochemical techniques can provide the preliminary activation of CO_2 that is required in the synthesis process, also, the electrochemical fixation of CO_2 might be of practical interest in the storage of solar energy.[21]

Up to now, most of the electrochemical synthesis of DMC from CO_2 and methanol involve the usage of supporting electrolytes,[16, 22] ionic liquids and toxic organic solvents (MeCN, DMF, etc.), which make the systems very complicated, inhibit the isolation of products and the recovery of solvents, and prohibit the demands of environmentally benign technologies as well.[22] Recently, a new divided electrochemical reactor has been investigated to avoid the addition of carcinogenic compounds,[16] but the liquid electrolyte (1-butyl-3-methylimidazolium bromide) was still required. Besides, the electrochemical techniques had to overcome the difficulties of finding electrodes with high electrocatalytic activity and improving the CO_2 solubility in aqueous solutions. A possible method to resolve these problems is to perform the electrochemical process in nonaqueous solutions or under high pressure.[21] Based on the research on the electrocatalytic apparatus by Yamanaka [23] and Ampelli,[24] our group [25] designed a new electro-assisted catalytic device for the direct DMC formation from CO_2 and methanol. The newly invented cell reactor is similar to a plate capacitor. It not only makes the electrochemical reaction system be simple but also facilitates the separation of catalysts with products, which in turn is good for the recycle of catalysts.

Amines are widely used for the CO_2 fixation and there are a number of references in which they are also employed as catalysts in the reaction involving the electrochemical reduction of CO_2.[26] Furthermore, amines are attractive as catalysts for the DMC formation because they can easily cooperate with CO_2 and methanol to form the effective intermediate.[27] 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) as a nucleophilic base have been widely explored in the fixation of CO_2 to form the DBU-CO_2 complex.[26-29] However, using DBU as catalyst has some drawbacks that it could not be reused and has an unpleasant flavor during the operational process. To overcome these problems and prompted by our wish for the electrochemical activation of CO_2 and methanol under solvent-free conditions, we loaded DBU on carbonaceous materials.

In this paper, we first report the electrochemical activation of CO_2 and methanol for the direct DMC formation without using any electrolytes or solvents over carbonaceous materials supported DBU. The experiments were processed on the new electro-assisted catalytic device assembled by our group, which enables the electrochemical reaction system be simple, promotes the separation of catalysts with products, and it is also beneficial for the recycle of catalysts. The influences of various applied voltage modes and conductivities of catalysts on the catalytic performances were investigated. Moreover, the recyclability of the catalysts was also explored.

2．Experimental

2.1 Catalysts preparation

Carbonaceous materials including nature graphite (NC), active carbon (AC), expanded graphite (EG) and graphite oxide (GO) were used as catalyst carriers. The NC, AC and EG received from commercial suppliers were treated by 5% HCl to remove the impurities. The GO

was synthesized according to the Hummer's method [30]. The DBU was loaded by the impregnation method. The DBU was first dispersed in methanol, and then mixed with carbonaceous materials, respectively. The samples are denoted as DBU-NC (or AC, EG, GO). The excessive methanol was evaporated at 40 °C under vacuum, followed by drying at 80 °C overnight. The loading weight of DBU to the catalyst carriers is 15 wt%.

2.2 Electro-assisted catalytic apparatus

The catalytic evaluation was carried out on the electro-assisted catalytic apparatus, [25] and its configuration was illustrated in **Scheme 1**. The setup was composed of a cell reactor (with voltage or without voltage, it could be selected freely), voltage generator，a mass flow controller of CO_2, a methanol bubbler, a six-way valve, a back-pressure regulator and a gas chromatography (GC7890). The cell reactor and the six-way valve were placed into an oven. The oven and cell reactor were each equipped with a thermometer, measured by thermocouples. The system pressure was determined by a pressure sensor and controlled by back-pressure regulator.
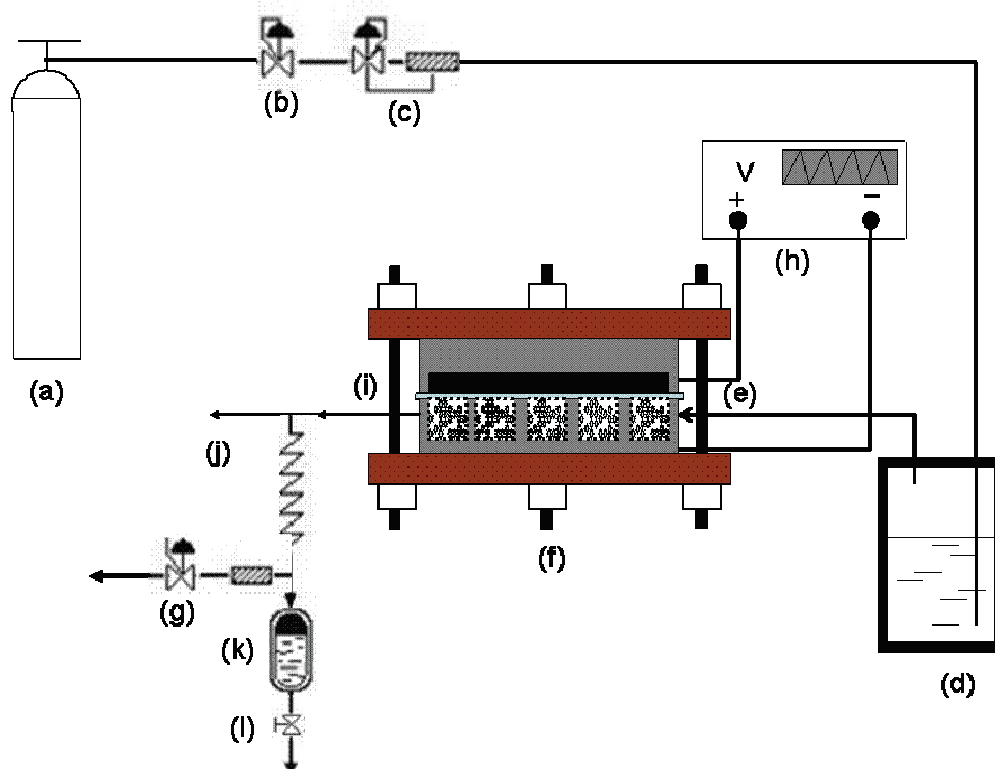
Scheme 1 Diagram of apparatus for the synthesis of DMC: (a) CO_2 gas cylinder; (b) Pressure

regulator; (c) Mass flow controller; (d) Bubbler (methanol); (e) Reactants inlet port; (f) Cell

Reactor; (g) Back-pressure regulator; (h)   Voltage generator (CHI600D electrochemical

station); (i) Outlet port; (j)   a six-way valve and GC (7890); (k) Cooling separator; (l) Cut-off

valve

The cell reactor similar to a plate capacitor is composed mainly of a positive and negative

electrode plates, which are made from corrosion resistant stainless steel. The negative

electrode plate is engraved with a recess as the catalyst bed. The intake port and outlet are

provided at both ends of the recess respectively. There is also a recess engraved on the positive

electrode plate, which is filled with activated carbon and encapsulated with insulating

diaphragm. In order to get a symmetric capacitor-like reactor, the activated carbon

corresponding to the catalyst bed in the cathode was filled in the anode. The insulating

membrane in the apparatus was polyethylene terephthalate (PET), which is used to separate the anode and cathode, thus a well electric field could be formed between the anode and the cathode. The two electrode plates were spaced from the insulating membrane, and the package can be sealed by tightening the bolts. Schematic diagrams of two electrode plates and the cell reactor are shown in **Scheme 2, Scheme 3 and Scheme 4.**
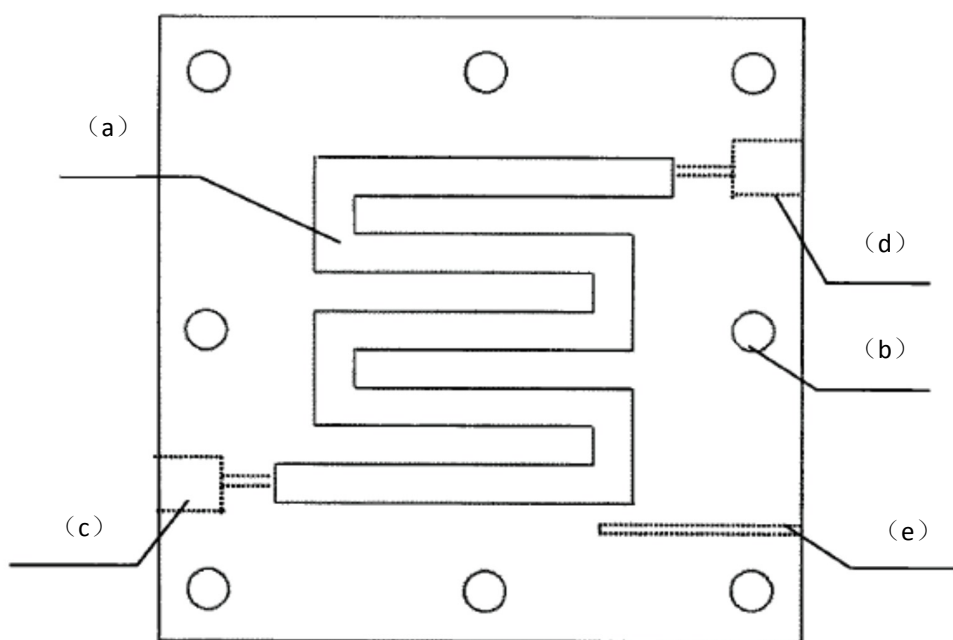
Scheme 2 Negative electrode plate of the cell reactor: (a) Catalysts bed recess; (B) Bolt hole; (c) Reactants inlet port; (d) Outlet port; (e) Thermocouple slot
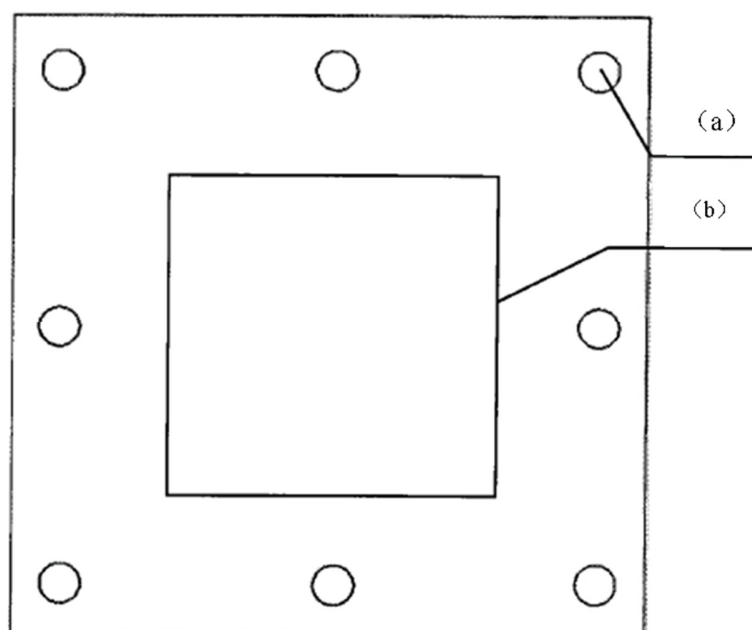
Scheme 3 Positive electrode plate of the cell reactor: (a) Bolt hole; (b) Recess filled with activated

carbon and encapsulated with insulating diaphragm
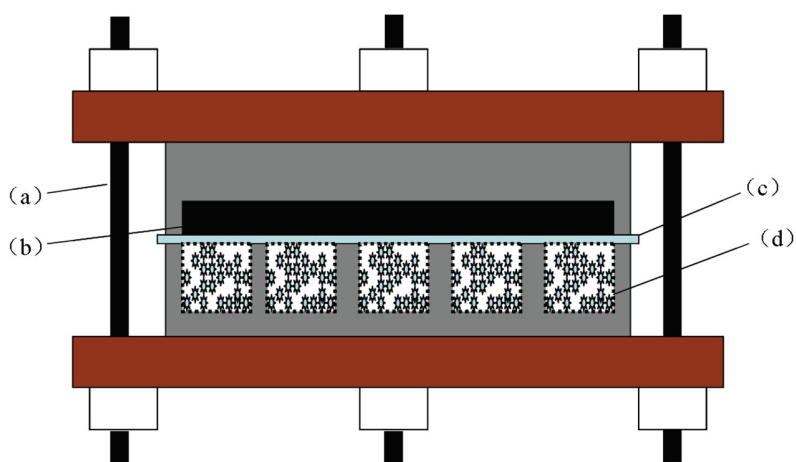
Scheme 4 Cell reactor: (a) The bolts; (b) Active carbon (AC); (c) Insulating diaphragm; (d)

catalysts

2.3 Catalyst characterization

Thermogravimetric analysis (TGA) were recorded on a Perkin-Elmer Pyris Diamond SII

thermal analyzer. Samples were heated over a range of 50 to 600 °C under a high purity N_2 flow

at a controlled heating rate of 10 °C/min.The X-ray diffraction (XRD) patterns were recorded

on a Rigaku D-Max 2200 diffractometer with Bragg-Brentano θ-2θ geometry (40 kV and 30

mA), using graphite monochromatized Cu Kα radiation. Fourier transform infrared (FTIR)

spectra of the samples were recorded on an Analect RFX-65A type FTIR spectrometer using

KBr pellet samples.The conductivities of different catalysts were characterized by four-probe

conductivity tester (SDY-4). The catalysts were pressed into a circular plate before the

measurements.

2.4 Catalytic evaluations

5g Fresh catalysts are compactly loaded in the groove of the negative electrode plate, an

insulating membrane was placed between the two electrode plates. After the two electrode plates

were sealed by the polytetrafluoroethylene film frame, then tightening the bolts. The schematic

diagram of the final package of the cell reactor with catalysts are shown in **Scheme 4**. The

voltages on the cell reactor were supplied by the CHI600D electrochemical station (Shanghai

Chenhua Instrument Company). Several types of voltage modes were applied to the cell reactor,

including constant, triangular wave, square wave and sawtooth wave voltages. The constant

voltage changes from 3V to 9V, while the latter three types change from 0 to 10V, and the periods

are ten minutes for each of them. The voltage modes are presented in **Fig.1**.
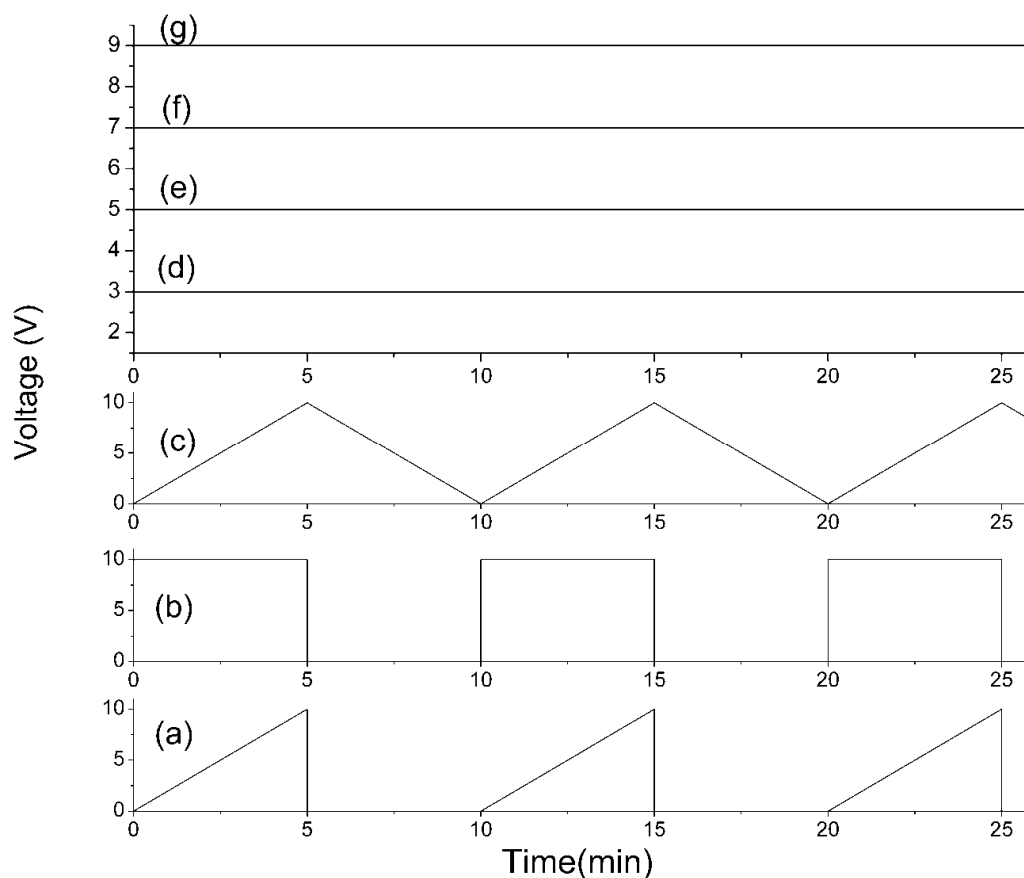
Fig.1 Different types of voltage modes applied to the cell reactor: (a) sawtooth wave voltages; (b) square wave voltages; (c) triangular wave voltages; (d) constant voltage (3V); (e) constant voltage (5V); (f) constant voltage (7V); (g) constant voltage (9V)

Methanol was introduced by the passage of the CO_2 carrier gas through a saturator maintained at 35 °C. Methanol-saturated CO_2 stream was passed into the reactor. The formation of DMC from CO_2 and methanol was carried out subsequently under the desired reaction conditions: Pressure (P): 0.6 MPa, Temperature (T): 120 °C, Space Velocity (SV): 540h^{-1}. All the effluent gases were analyzed by gas Chromatographs (GC) equipped with a flame ionization detector (FID). The condensed liquid collected by the cooling separator was

analyzed by the gas chromatograph mass spectrometer (GCMS-QP2010 plus) to confirm the

DMC formation in this reaction. The main reaction products of CO_2 reacting with methanol

over the catalysts were DMC and H_2O, and there were a few by-products of CH_2O, CO and

dimethyl ether (DME). The detailed analysis method of the final product was reported

elsewhere.[14]

3. Results and discussion

3.1 Catalyst Characterizations

From the TGA data presented in **Fig.2**, the first weight loss below 100 °C is assigned to the

surface adsorbed water on the catalysts. It seems that the final loading weight percent of DBU

on the AC is ca.15 wt%, which is consistent with the DBU amount as the prepared the catalysts.
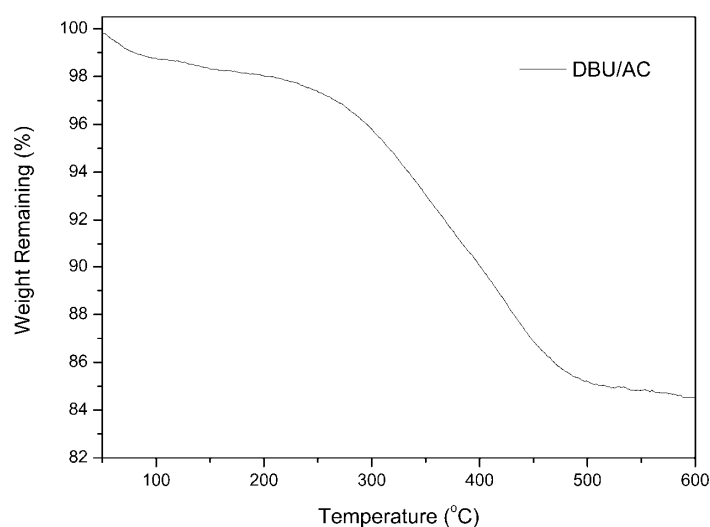

Fig.2 TGA profile of the DBU/AC.

From the FTIR analysis presented in **Fig. 3**, there are new IR peaks after DBU is loaded

compared with the pristine carbonaceous materials. The IR vibration located at ca. 1570 cm^{-1} is

believed to assign to C=N, and the peaks at around 1445, 1320 and 1200 cm⁻¹ are probably the result of the IR vibration of the C-N bonds in DBU.[31] For the FTIR of DBU-GO, the IR peak located at around 1721 cm⁻¹ belongs to C=O become intense and broader by comparison with neat GO, and this suggests that the DBU might interacted with the –COOH groups on the surface of GO nanosheets to form a chemical bond.[32]
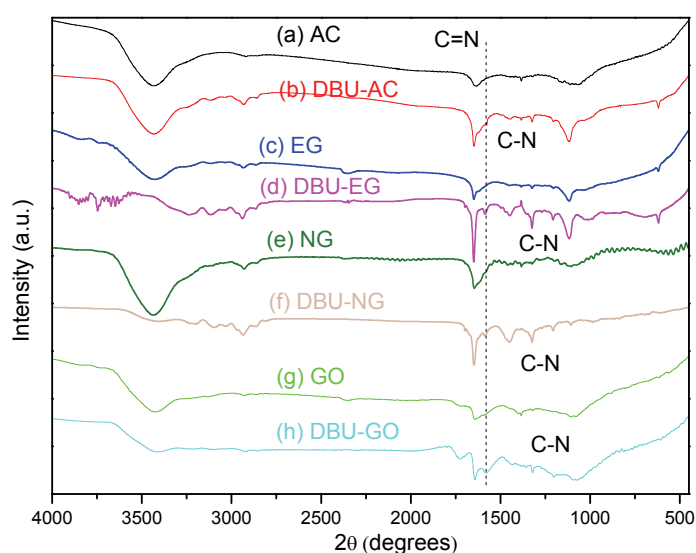
Fig. 3 FTIR analysis of carbonaceous materials with and without DBU.

The XRD patterns of carbonaceous materials with and without DBU are presented in **Fig.4**. It is observed that only the GO greatly altered its structure after the DBU was loaded. It can be concluded that the DBU might be physically mixed with the pristine the AC, EG and NG. For the DBU-GO, the diffraction peak assigned to the interlayer spacing of GO located at ca. 10.6° shifted to a lower value, and a broad diffraction peak at ca. 19.0° appear. These information

provide evidence that the DBU is successfully attached onto the GO nanosheets during the impregnation process.[33] These are in consistent with the FTIR analysis.
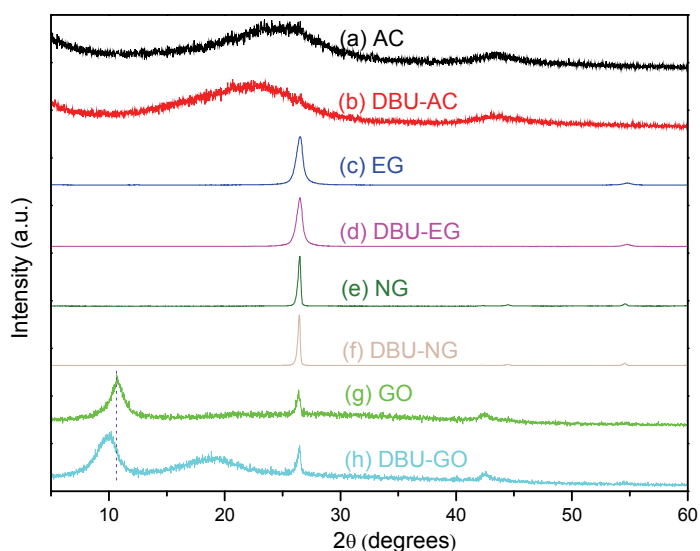

Fig. 4 XRD patterns of carbonaceous materials with and without DBU.

3.2 Catalytic performances

Table 1 Effects of applied voltage modes on the catalytic performances of DMC formation over 15wt%DBU/AC

Applied Voltage Modes	Methanol Conversion (%)	DMC Selectivity (%)	Yield %
No Voltage	1.88	85.8	1.61
Sawtooth Wave	2.81	90.4	2.54
Square Wave	3.37	91.5	3.08
Triangular Wave	3.00	89.2	2.68
Constant（3V）	3.65	87.8	3.20
Constant（5V）	3.77	88.3	3.33
Constant（7V）	3.89	89.5	3.48
Constant（9V）	3.15	90.6	2.85

The data listed in the table are the average value obtained between 2-4 h with time on stream for 5 h. Reaction conditions: Pressure: 0.6 MPa, Temperature: 120 °C, Space velocity: 540 h^{-1}, catalyst amount: 5 g; DBU loading weight: 15 wt%.

The catalytic activities of DBU/AC with different applied voltage modes are presented in **Table 1**. Different DMC yields over electro-assisted catalysts were found with different working voltage modes. The constant working potential exhibits better catalytic activity than the metabolic voltages. Besides, the catalyst activities with the constant voltage first increase and then decrease with increasing voltage values, which can be inferred that there is an optimal voltage to activate the reactants both CO_2 and methanol for the electro-assisted generation of DMC. The maximum methanol conversion of 3.89% with DMC selectivity of 89.5% could be obtained when the constant voltage of 7 V was applied.

Table 2 Influences of catalyst carriers on the electro-assisted DMC formation from CO_2 and methanol

Catalyst Support	Conductivity $(S \cdot m^{-1})$	Voltage (V)	Methanol Conversion (%)	DMC Selectivity (%)	Yield %
AC	100.00	0	1.88	85.8	1.61
		7	3.89	89.5	3.48
EG	28.09	0	1.64	90.3	1.48
		7	2.98	91.4	2.72
GO	27.70	0	1.52	89.6	1.36
		7	2.81	90.2	2.53
NC	80.65	0	1.76	89.5	1.58
		7	3.69	90.9	3.35

The data listed in the table are the average value obtained between 2-4 h with time on stream for 5 h. Reaction conditions: Pressure: 0.6 MPa, Temperature: 120 °C, Space velocity: 540 h^{-1}, catalyst amount: 5 g; DBU loading weight: 15 wt%.

Table 2 shows the results of the electro-assisted DMC formation over DBU loaded on different catalyst carriers. Obviously, the addition of voltages on the catalysts obviously

increases the catalytic performances of each catalyst. Besides, the catalytic activities vary with different catalyst support, and the higher conductivity results in a superior catalytic performance for the electro-assisted DMC formation.

To ensure that the catalysts can be recycled by using the cell reactor, we recovered the used catalysts under N_2 atmosphere at 150 °C for 3 h to remove the debris of activated species and byproducts adsorbed on the surface of the catalyst, and then they were reused for the DMC formation. This process was repeated three times, and the experimental results are presented in **Table 3**. Obviously, the catalysts were recyclable, but the DMC yield decreased gradually with the increase of the number of recycles. When the catalysts were reused up to three times, the methanol conversion decreased to 1.86% with DMC selectivity of 87.8%. The recession of the catalytic performance of the recycled catalysts may be due to deactivation of active components during the process of re-activation of the catalysts.

Table 3 Recyclability of the 15%DBU/AC for the electro-assisted DMC formation from CO_2 and methanol.

| Recycle times	Methanol Conversion (%)	DMC Selectivity (%)	Yield %
Fresh	3.89	89.5	3.48
1	3.25	89.2	2.90
2	2.71	88.1	2.38
3	1.86	87.8	1.63

The data listed in the table are the average value obtained between 2-4 h with time on stream for 5 h. Reaction conditions: Pressure: 0.6 MPa, Temperature: 120 °C, Space velocity: 540 h^{-1}; Catalyst amount: 5g; Voltage mode: Constant voltage (7V).

3.3 Discussion

The catalytic reactor used in our experiment is similar to a plate capacitor, and the catalyst bed is placed in the negative electrode plate. There should be plenty free electrons in the catalyst bed when the voltages are applied to the catalytic reactor. The free electrons will be transferred towards carbon dioxide under the action of electric fields in the conductive carriers, which may electrically activate the reactant adsorbed on the catalysts. From the experimental results presented in **Table 1** and **Table 2**, the changes in the voltage and its mode on the catalysts can obviously enhance the catalytic performances. Moreover, the catalyst support can also affect the catalytic activity. The constant voltages show good catalytic activities relatively compared to other voltage modes. Presumably, this is due to the steady streams of free electrons in the catalyst bed provide at a constant voltages. In addition, the catalytic activities vary with different catalyst carriers could be explained by diverse conductivities of the catalysts. As it is well known that the conductivity influences the speed of free electron transfer, a lower conductivity will limit the transfer of the free electrons in catalyst bed. This is why a higher conductivity results in a better catalytic performance of electro-assisted DMC formation. These findings indicate that the speed of electron transfer in the catalyst bed plays a key role in determining the catalytic performance.

It has been reported by many researchers[21, 34-37] that CO_2 can capture one electron and be electrochemically reduced to CO_2^- radical ($(CO_2)_{ad}+e^-\rightarrow(CO_2^-)_{ad}$) on the flat metallic cathode. On the other hand, CH_3OH[38] can be electro oxidized into $(CH_3O^+)_{ad}$ and H^+ radicals ($CH_3OH+e^-\rightarrow(CH3O^-)_{ad}+H^++e^-$). According to the literatures, CO_2 and DBU can easily form the zwitterionic complex through the coordination of an N-CO_2 bond,[26] which could further generate alkyl carbonate ammonium compound [39] in the presence of methanol. Based on the

excellent work of other researchers and our experimental data, we proposed the reaction

mechanism of the electro-assisted DMC formation from CO_2 and methanol over the

carbonaceous materials supported DBU as catalysts, and it is outlined in **Scheme 5** and

Scheme 6: the CO_2 and methanol adsorbed on the catalysts are initially electrochemically

activated to form the CO_2^- and CH_3O^- radicals, respectively. Then CO_2^- coordinated with

DBU to form an ion-pairing complex, and quickly form the alkyl carbonate ammonium

compound by reacting with methanol. Then, the electrical activation species CH_3O^- of

methanol further cooperate with alkyl carbonate ammonium compound to get the final

product DMC and simultaneously release a molecular water. The electrocatalysis improve

the efficiency of activation of CO_2 and methanol, which to some extent will enhance the

catalyst activity.
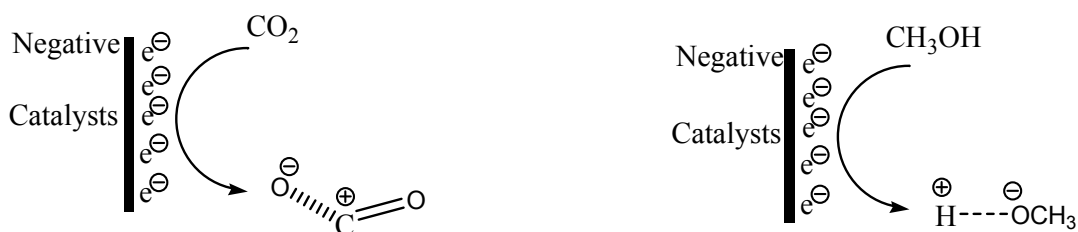
Scheme 5 Electro-activation of CO_2 and methanol adsorbed on the catalysts
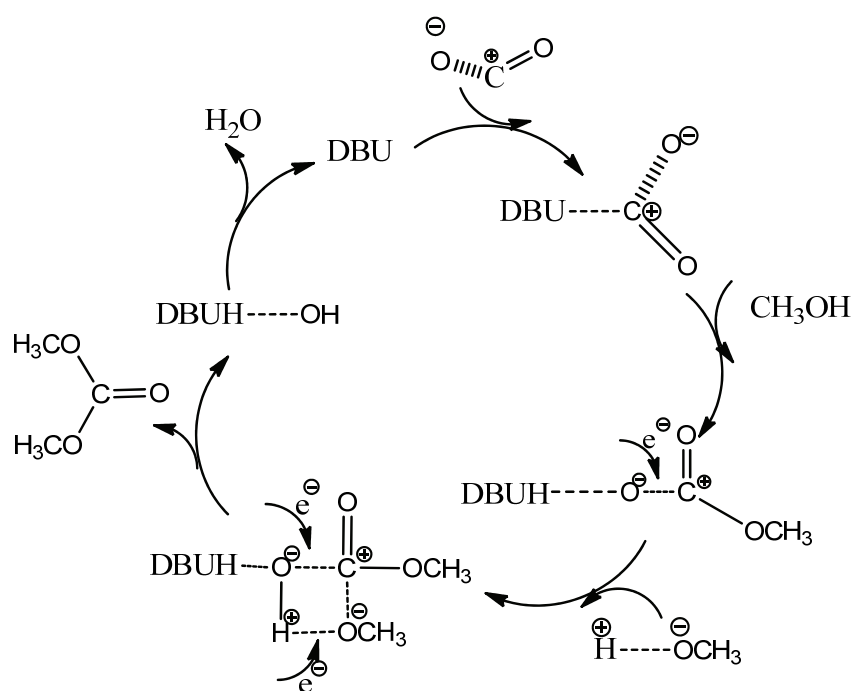
Scheme 6 Proposed reaction mechanism of the electro-assisted DMC formation from

CO_2 and methanol over carbonaceous materials supported DBU

4. Conclusions

In summary, an electrochemical activation of CO_2 and methanol for the direct DMC

formation under solvent-free conditions over carbonaceous materials supported DBU on the

plate capacitor-like cell reactor invented by our group was firstly proposed. The influences

of applied voltage modes and various catalyst carriers on the catalytic performances were

examined. It was found that constant voltages exhibited superior catalytic performances than

the fast-changed waves of voltages, and the catalysts with higher conductivities presented

better catalytic activities. The catalytic performance can be greatly enhanced with the

addition of voltages. The methanol conversion can be improved from 1.88% with no voltages

to 3.89% with a constant voltage of 7V applied to the catalyst bed over the DBU loaded on

AC. In addition, the supported DBU as assistant catalysts demonstrated readily recovery property and excellent recyclability on our electrochemical cell reactor. Based on the experimental data and other researchers' excellent work, we proposed the reaction mechanism of the electrocatalysis for DMC formation. The efficiency of the activation of CO_2 and methanol can be enhanced when the voltages are applied, and this might be the major reason for the higher catalytic performances compared with no voltage involved. In a word, our protocol for the electro-assisted DMC formation shows notable advantages, such as simple manipulation of the reaction system, ease of separation of products with catalysts, non-solvent reaction medium, as well as the recycle of catalysts. These factors exhibit the potential benefit of industrial application.
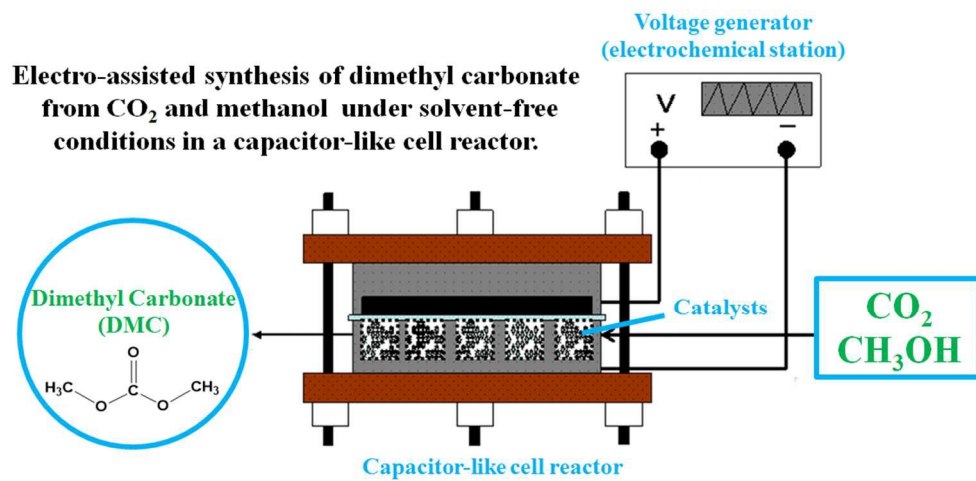
5. Acknowledgments

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Electro-assisted synthesis of dimethyl carbonate from CO_2 and methanol under solvent-free conditions in a capacitor-like cell reactor.

Voltage generator (electrochemical station)

Dimethyl Carbonate (DMC)

Catalysts

CO_2
CH_3OH

Capacitor-like cell reactor

304x158mm (96 x 96 DPI)