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Highly regioselective electrochemical synthesis of dioic acids from dienes and carbon dioxide

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ABSTRACT

A simple and efficient electrochemical method has been developed for highly regioselective synthesis of unsaturated 1,6-dioic acids from 1,3-dienes and CO_2. The electrosynthesis was successfully carried out by using a nickel cathode and an aluminum anode in an undivided cell containing *n*-Bu_4NBr-DMF electrolyte with a constant current under 3 MPa pressure of CO_2, and the sole 1,4-addition products were obtained in good to excellent yields. The plausible mechanism for electrodicarboxylation reaction of 1,3-butadiene with CO_2 was discussed briefly. In addition, further research shows that 3-hexene-1,6-dioic acid could be easily converted into adipic acid via the electroreduction in the diluted H_2SO_4 solution.

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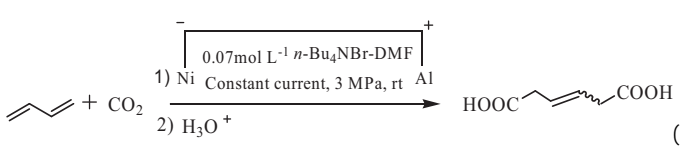
1. Introduction

The electrochemical fixation of CO_2 into unsaturated hydrocarbons has received much attention and become an interesting topic in synthetic organic chemistry [1–3]. From an environmental viewpoint, CO_2 is a renewable, low cost, abundant and nontoxic C_1-synthon [4–7]. The fixation and conversion of CO_2 are beneficial to environment. From the viewpoint of synthetic methodology, electrochemical process is one of green, atom-economical and efficient processes because no harmful wastes are generated along with production of desired compounds. Especially, the carboxylic acids obtained via the electrochemical fixation of CO_2 are usually important synthetic intermediates in organic synthesis and the production of polymer materials or pharmaceuticals [8]. Up to now, many efforts have been devoted to the investigation on the electrocarboxylation of CO_2 with various organic compounds including alkenes [1,9–12], alkynes [3,13], ketones [14–17], halides [18–25], imines [26], epoxides [27–29] and dienes [30–35]. It is worth noting that the electrocarboxylation of 1,3-butadiene aimed at synthesizing adipic acid [36–38], one of the most important industrial chemicals, has been one of the most topical problems in synthetic electroorganic chemistry for more than 30 years [33]. Until now, the electrochemical reaction between CO_2 and 1,3-butadiene often led to the generation of a complicated mixture containing 3-pentenoic acid, 4-pentenoic acid, 2-ethylsuccinic acid and 3-hexene-1,6-dioic acid [35]. Therefore, it is still necessary to exploit an efficient electrochemical route for the synthesis of 3-hexene-1,6-dioic acid from 1,3-butadiene and CO_2.

Al and Mg as sacrificial anodes have been widely used in undivided cells for the electrocarboxylation process of organic compounds with CO_2. Some researches showed that Al^{3+} or Mg^{2+} ions formed on the anode or added to the cell could strongly affect the processes of electrocarboxylation [39,40], and that moderate and high pressure of carbon dioxide are favorable for the electrocarboxylate processes [27,41,42].

We previously developed an efficient electrochemical route with Ni cathode for the dicarboxylation of arylacetylenes or aryl-substituted alkenes with CO_2 in an undivided cell at room temperature [41,42]. Inspired by the successful results, we further investigate the feasibility of the electrochemical route for the synthesis of 3-hexene-1,6-dioic acid, a precursor of adipic acid, using 1,3-butadiene and CO_2 as raw materials in the absence of additional catalysts. Fortunately, 3-hexene-1,6-dioic acid as the sole product in 84% yield is achieved under the optimum conditions Eq. (1). In this paper, we report the approach of the electrosynthesis of various unsaturated dicarboxylic acids in good to excellent yields for potential industrial application.



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2. Experimental

2.1. Chemicals

N,*N*-Dimethylformamide (DMF) (Alfa Aesar, AR) was kept over anhydrous $MgSO_4$ for several days. Tetrabutyl ammonium bromide (n-Bu_4NBr) (Alfa Aesar, AR) was dried at 60 °C under vacuum for 10 h. Other dienes (AR) were all purchased from Alfa Aesar and were used without further purification. 1,3-butadiene was purchased from Guangzhou Petrochemicals Co. Ltd.

2.2. Instrumentation

The electrolytic cell is the same as that reported previously [41]. FTIR spectra were measured by a TENSOR27 spectrometer. ^{1}H NMR and ^{13}C NMR were determined on a Bruker DRX-400 spectrometer with DMSO-d_6 as the solvent in the presence of $SiMe_4$ as an internal standard. Mass spectral analyses were done on a Shimadzu QP5050A spectrometer.

Prior to the cyclic voltammetry (CV) experiment, the electrodes were cleaned by diluted hydrochloric acid and carefully washed with distilled water, and finally dried. The working electrode and counter-electrode (Al) were built with the same size (2 mm × 2 cm, Alfa Aesar, 99.999%). CV experiments were carried out at an Auto LAB (PGSTAT 30) electrochemical workstation, with Ni or Ag as a working electrode and a saturated calomel electrode (SCE) as a reference electrode. The solution was saturated with CO_2 (0.1 MPa) during the CV experiments.

2.3. The electrocarboxylation of 1,3-butadiene with carbon dioxide

Before the electrosynthesis, the anode and cathode were cleaned with detergent and diluted hydrochloric acid, followed by washing with distilled water and then dried. The electrosynthesis was carried out in the high-pressure stainless-steel undivided cell fitted with a nickel sheet cathode (wet surface area 6 cm^2) and an aluminum sheet anode (wet surface area 6 cm^2). In a typical experimental procedure, dried DMF (*N*,*N*-dimethylformamide) solvent (35 mL) and n-Bu_4NBr (2.5 mmol) were added to the cell, respectively. After the electrochemical cell was sealed, 1,3-butadiene (gas) was charged to reach the saturated state. The accurate quantity of 1,3-butadiene was determined according to its amount dissolved in DMF solvent after superfluous 1,3-butadiene was discharged from the cell. Then, CO_2 was charged into the cell to the desired pressure. The electrosynthesis was carried out under continuously stirring at room temperature until electricity 4 F mol^{-1} of starting substrates had been passed through the cell. After the electrolyte was distilled at reduced pressure, the residue was acidified with hydrochloric acid (2 mol L^{-1}), then continuously stirred for 6 h, and extracted with diethyl ether (3 × 25 mL). The ether phase was washed twice with distilled water and dried with anhydrous $MgSO_4$. After evaporation of ether, the obtained yellow crude product was dried in a vacuum oven at 45 °C for 5 h, and recrystallized twice with ethyl acetate–petroleum ether, and dried at 60 °C in a vacuum oven.

2.4. The electroreduction of 3-hexene-1,6-dioic acid into adipic acid

At room temperature, the as-prepared 3-hexene-1,6-dioic acid (20 mmol) and H_2SO_4 aqueous solution (1 mol L^{-1}, 40 mL) were added to the undivided cell (100 mL) fitted with Ni cathode (wet surface area 4 cm^2) and Pt anode (wet surface area 4 cm^2). In a typical experiment, the electroreduction was performed at 60 °C under continuously stirring until electricity 3 F mol^{-1} of starting substrates had been passed through the cell. At the end of the electrolysis, the electrolyte was cooled to room temperature, accompanied by the precipitation of a large amount of adipic acid. After filtered, the crude adipic acid was obtained and recrystallized twice with ethanol–petroleum ether, then dried at 60 °C in a vacuum oven. In addition, mother liquor can be recycled.

2.5. Characterizations of products

Spectroscopic data of the prepared compounds were given as follows.

(*Z*)-*3-hexene-1,6-dioic acid*: IR (neat): ν: 3480 (OH), 1700 (C=O) cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 12.2 (s, 2H), 5.62–5.64 (m, 2H), 3.02 (d, J = 4.4 Hz, 4H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 172.9, 125.1, 33.2. MS (EI): m/z 144 (M$^+$).

(*E*)-*3-hexene-1,6-dioic acid*: IR (neat): ν: 3450 (OH), 1700 (C=O) cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 12.2 (s, 2H), 5.57–5.59 (m, 2H), 2.99 (d, J = 13.4 Hz, 4H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 173.2, 126.5, 37.9. MS (EI): m/z 144 (M$^+$).

(*E*)-*3-methyl-3-hexene-1,6-dioic acid*: IR (neat): ν: 3426 (OH), 1690 (C=O) cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 12.2 (s, 2H), 5.39 (t, J = 8 Hz, 1H), 2.99 (d, J = 8 Hz, 2H), 2.95 (s, 2H), 1.63 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 173.0, 172.7, 131.8, 120.8, 44.5, 33.5, 16.6. MS (EI): m/z 158 (M$^+$).

(*E*)-*3,4-dimethyl-3-hexene-1,6-dioic acid*: IR (neat): ν: 3424 (OH), 1695 (C=O) cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 12.1 (s, 2H), 2.29 (s, 4H), 1.68 (s, 6H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 172.7, 125.4, 41.2, 19.3. MS (EI): m/z 172 (M$^+$).

(*E*)-*2,5-diphenyl-3-hexene-1,6-dioic acid*: IR (neat): ν: 3409 (OH), 1696 (C=O) cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): 12.1 (s, 2H), 7.21–7.33 (m, 10H), 5.93 (dd, J_1 = 2.4 Hz, J_2 = 5.2 Hz, 2H), 4.33 (dd, J_1 = 2.4 Hz, J_2 = 5.2 Hz, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 173.7, 139.5, 130.9, 129.0, 128.2, 127.4, 54.2. MS (EI): m/z 296 (M$^+$).

2-cyclohexene-1,4-dicarboxylic acid: IR (neat): ν: 3430 (OH), 1700 (C=O) cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 12.5 (s, 2H), 5.76–5.82 (m, 2H), 3.04–3.42 (m, 2H), 1.89–1.95 (m, 2H), 1.62–1.70 (m, 2H). ^{13}C NMR (DMSO-d_6, 100 MHz): δ 174.8, 126.9, 40.2, 23.8. MS (EI): m/z 170 (M$^+$).

3. Results and discussion

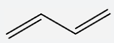
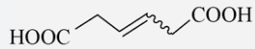
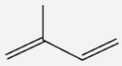
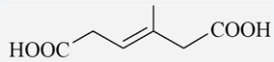
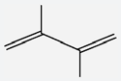
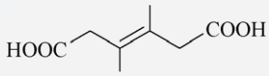
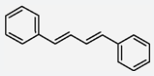
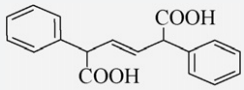
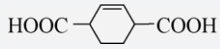
3.1. Electrosynthesis of 3-ene-1,6-dioic acids from dienes and CO_2

Under the optimum conditions (Ni cathode and Al anode, n-Bu_4NBr-DMF as electrolyte, the electricity 4 F mol^{-1} of starting substrates, CO_2 pressure 3 MPa), the electrochemical dicarboxylation of different 1,3-dienes were examined, and the results are listed in Table 1. All 1,3-diene substrates gave 1,4-addition products with high regioselectivity in good to excellent yields. Except for 1,3-butadiene, the configuration of the product corresponding to linear dienes is only *trans* form (Table 1, entries 2–4). Cyclohexadiene could be also converted into the corresponding dicarboxylic acids in good yield (70%, Table 1, entry 5). In addition, very small amount of polymers were found in our present experimental conditions.

3.2. Influence of cathode materials

1,3-Butadiene was selected as a model molecule to systemically investigate the influence of some key factors on the electrosynthesis. Some electrochemical parameters such as supporting electrolyte, temperature, substrate concentrations and current density have been discussed in details previously [41,42], which could provide some references for the present work. Here the effect of different electrode materials was first investigated on the electrocarboxylation of 1,3-butadiene with CO_2. As known, electrode materials are very important for electrochemical reactions.

Table 1
Electrocarboxylations of dienes with CO_2.[a]

Entry	Substrate	Product	Yield (%)[b]	η (%)[c]	Z:E[d]
1			84	42	1:1
2			80	40	0:100
3			87	43.5	0:100
4			90	45	0:100
5			70	35	–

[a] Experimental conditions: diene (6.9 mmol), DMF (35 mL), CO_2 3 MPa, room temperature, n-Bu_4NBr (2.5 mmol), electricity (4 F mol^{-1}), current density 10 mA cm^{-2}, Ni cathode and Al anode.
[b] Isolated yield based on dienes (6.9 mmol).
[c] $\eta = Q_1/Q_2$ (η: current efficiency; Q_1: quantity of electricity consumed in forming product; Q_2: total electricity quantity in the electrolysis).
[d] Ratio was determined by ^{1}H NMR analysis.

Metal Al is used as a sacrificial anode. So the investigation was focused on different cathode materials (Ag, Zn, Cu, Ni, stainless steel and Pt). Pt cathode gave 3-hexene-1,6-dioic acid in a very low yield (Table 2, entry 3). Especially, when Ag or Zn was used as cathode and the pressure of CO_2 was controlled under 3 MPa, only a small amount of 3-hexene-1,6-dioic acid was obtained, while the significant amount of carbonates were detected (Table 2, entries 1 and 2). The formation of carbonates could be explained on the basis of the stoichiometry ($2CO_2 + 2e^- \rightarrow CO + CO_3^{2-}$) as proposed by previous authors [43]. Very significantly, Cu, stainless steel and Ni cathodes could afford 3-hexene-1,6-dioic acid in good yields (Table 2, entries 4–6). It was also found that the target product 3-hexene-1,6-dioic acid was obtained in Z and E forms. This may be the result of less steric hindrance in the electrodicarboxylation reaction. Different cathode materials led to different results, which may be that the nature of electrode materials strongly influences the reduction of CO_2 or 1,3-butadiene [37]. Among these cathodes, Ni cathode displayed the best result. However, the current efficiency, in the case of Ni cathode, is only 42% (Table 2, entry 6). The reason may be that, in the present electrochemical system of high CO_2 pressure, CO_2 is easily reduced to transform into carbonates, which consumes most of the supplied electricity in the electrolysis. Thus, how to enhance the current efficiency is an urgent problem to be solved in the future.

To better understand the difference of these cathode materials, Ni and Ag were chosen as working electrodes to further investigate the CV of the electrolytic system under the same conditions. Figs. 1 and 2 show the CV behaviors of n-Bu_4NBr-DMF solution with Ni and Ag as working electrodes, respectively. In the absence of 1,3-butadiene and CO_2 (Fig. 1), the increase of reduction current at $E < -2.50$ V versus SCE should be due to the reduction of DMF solvent at the cathode. From Figs. 1 and 2, it can be seen that the results of Ag cathode is obviously distinguished from those of Ni electrode. In the case of Ag electrode, an obvious reduction peak appears at the reduction potential of −0.70 V to −1.0 V versus SCE (Figs. 1a and 2a and b). However, when N_2 was bubbled into the electrolyte, the reduction peak was disappeared (Fig. 1b). It can be inferred that the reduction peak in Figs. 1a and 2a and b belongs to the reduction of O_2 dissolved in DMF solvent. In the case of Ni electrode, a similar behavior could not be observed (Figs. 1c, 2c and 3), namely the reduction of O_2 did not occur under the same conditions. In our electrochemical system, there is more or less oxygen in DMF solvent. Since Ag cathode is very sensitive to oxygen, the electrocar-

Table 2
Influence of cathode materials on the electrocarboxylation of 1,3-butadiene with CO_2.[a]

Entry	Cathode material	Yield (%)[b]	η(%)[d]
1[c]	Ag	5	2.5
2[c]	Zn	10	5
3	Pt	22	11
4	Cu	59	29.5
5	Stainless steel	71	35.5
6	Ni	84	42

[a] Electrolytic conditions: room temperature, Al anode, 1,3-butadiene (6.9 mmol), DMF (35 mL), n-Bu_4NBr (2.5 mmol), current density 10 mA cm^{-2}, CO_2 3 MPa, and electricity 4 F mol^{-1}.
[b] Isolated yield based on 1,3-butadiene (6.9 mmol).
[c] The carbonate is the main product.
[d] Current efficiency.

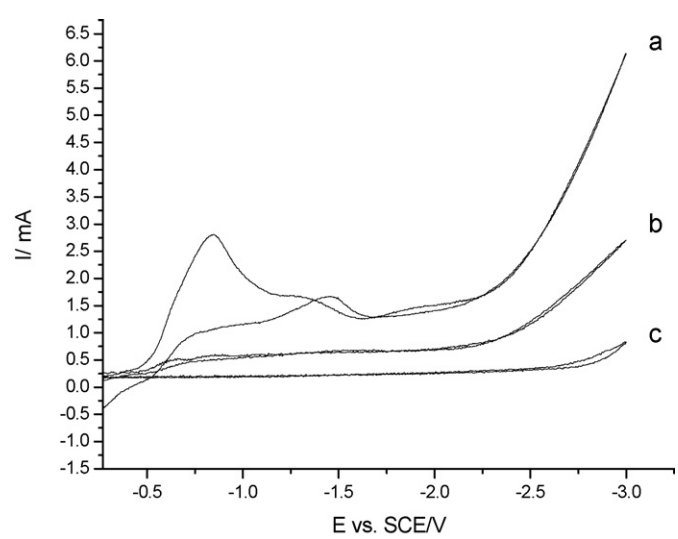


Fig. 1. Cyclic voltammograms of a 0.07 mol L^{-1} n-Bu_4NBr-DMF solution (35 mL) at room temperature (25 °C) at the scan rate 50 mV s^{-1} with different working electrodes: (a) Ag; (b) Ag (N_2 was bubbled into n-Bu_4NBr-DMF solution); and (c) Ni. The area of these two electrodes is the same.

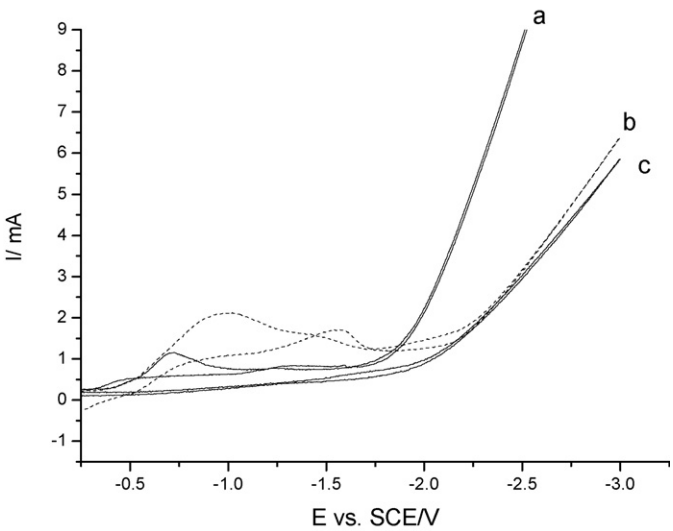


Fig. 2. Cyclic voltammograms of a 0.07 mol L^{-1} n-Bu$_4$NBr-DMF solution (35 mL) at room temperature (25 °C) at the scan rate 50 mV s^{-1} with different working electrodes: (a) Ag (in the presence of saturated CO_2 (0.1 MPa)); (b) Ag (in the presence of 1,3-butadiene of 6.9 mmol); and (c) Ni (in the presence of 1,3-butadiene of 6.9 mmol). The area of these two electrodes is the same. The oxygen dissolved in n-Bu$_4$NBr-DMF solution was not purged with N_2 in the all CV experiments.

boxylation of 1,3-dienes with CO_2 could be affected to some extent. The detailed role of different cathodes in the electrocarboxylation is needed to study further.

3.3. Influence of electricity and CO_2 pressure

During the electrochemical coupling reduction between 1,3-butadiene and CO_2, the yield of the target product strongly depends on the electricity (Q) supplied to the electrodes. As shown in Table 3, when the electricity passed the cell increased from 1 to 4 F mol^{-1}, the yield of the product increased rapidly from 20% to 84% (Table 3, entries 1–4). Further increasing the electricity, the yield of the target product increased slightly (Table 3, entry 5).

As CO_2 pressure increased from 1 to 3 MPa, the yield of the target product increased (Table 4, entries 1–3). Higher CO_2 pressure

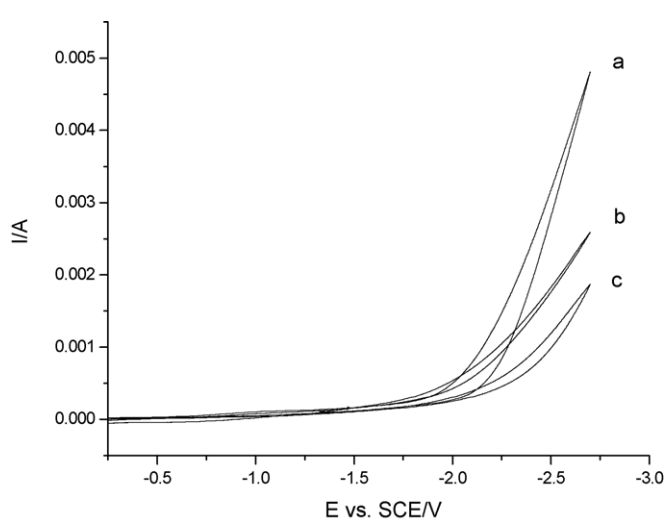


Fig. 3. Cyclic voltammograms of n-Bu$_4$NBr-DMF solutions (35 mL, 0.07 mol L^{-1}) at room temperature (25 °C) at the scan rate 50 mV s^{-1} with Ni as a working electrode: (a) only addition of 6.9 mmol 1,3-butadiene; (b) with the simultaneous presence of 6.9 mmol of 1,3-butadiene and saturated CO2 (0.1 MPa); and (c) only in the presence of saturated CO_2 (0.1 MPa).

Table 3
Influence of electricity on the electrocarboxylation of 1,3-butadiene with CO_2.[a]

Entry	Electricity (F mol^{-1})	Yield (%)[b]	η (%)[c]
1	1	20	40
2	2	49	49
3	3	70	46.7
4	4	84	42
5	5	87	34.8

[a] Electrolytic conditions: room temperature, 1,3-butadiene (6.9 mmol), DMF (35 mL), n-Bu$_4$NBr (2.5 mmol), current density 10 mA cm^{-2}, CO_2 pressure 3 MPa, Ni cathode and Al anode.
[b] Isolated yield based on 1,3-butadiene (6.9 mmol).
[c] Current efficiency.

Table 4
Influence of CO_2 pressure on the electrocarboxylation of 1,3-butadiene with CO_2.[a]

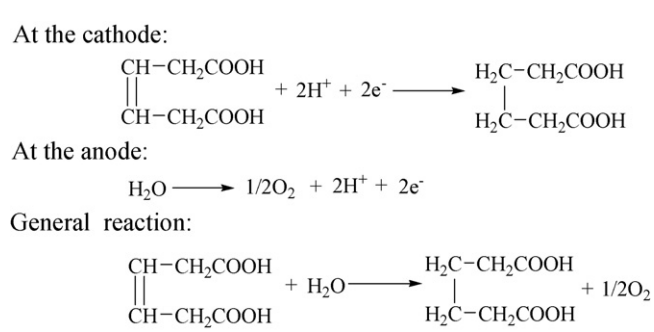
Entry	CO_2 pressure (MPa)	Yield (%)[b]	η (%)[c]
1	1	65	32.5
2	2	83	41.5
3	3	84	42
4	4	83	41.5
5	5	82	41

[a] Electrolytic conditions: room temperature, 1,3-butadiene (6.9 mmol), DMF (35 mL), n-Bu$_4$NBr (2.5 mmol), current density 10 mA cm^{-2}, and electricity 4 F mol^{-1}, Ni cathode and Al anode.
[b] Isolated yield based on 1,3-butadiene (6.9 mmol).
[c] Current efficiency.

favors to the electrochemical dicarboxylation of 1,3-butadiene with CO_2, which is in agreement with those of electrocarboxylations of epoxides or aryl-substituted alkenes with CO_2 under high CO_2 pressure [27,41]. The reason may be that enhancing CO_2 pressure can increase the solubility of CO_2 in DMF solvent, which results in increasing the yield of the product. When CO_2 pressure increased from 3 to 5 MPa, the yield almost unchanged (Table 4, entries 3–5). In fact, the amount of CO_2 in DMF solvent even at 2 MPa greatly exceeds that of 1,3-butadiene, so the effect of CO_2 pressure from 3 to 5 MPa on the electrodicarboxylation becomes negligible. On the contrary, further increasing CO_2 pressure may bring some negative effects on the electrosynthesis, such as the raise of the voltage between the anode and cathode, and the increase of by-product carbonates.

3.4. The electroreduction of 3-hexene-1,6-dioic acid into adipic acid

We further investigated the electroreduction of 3-hexene-1,6-dioic acid into adipic acid. The electroreduction was carried out in an undivided cell containing 1 mol L^{-1} H_2SO_4 electrolyte with Ni cathode and Pt anode, the electroreduction principle of 3-hexene-1,6-dioic acid as shown in Scheme 1.



Scheme 1. The electroreduction of 3-hexene-1,6-dioic acid into adipic acid.

Table 5
Influence of temperature on the electroreduction of 3-hexene-1,6-dioic acid into adipic acid.[a]

Entry	Temperature (°C)	Yield (%)[b]	η (%)[c]
1	20	23	15.3
2	40	48	32
3	60	65	43.3
4	70	68	45.3
5	80	67	44.6

[a] Electrolytic conditions: 3-hexene-1,6-dioic acid (20 mmol), H_2SO_4 (40 mL, 1 mol L^{-1}), current density 8 mA cm^{-2}, and electricity 3 F mol^{-1}, Ni cathode and Pt anode.
[b] Isolated yield based on 3-hexene-1,6-dioic acid (20 mmol).
[c] Current efficiency.

Table 6
Influence of electricity on the electroreduction of 3-hexene-1,6-dioic acid into adipic acid.[a]

Entry	Electricity (F mol^{-1})	Yield (%)[b]	η (%)[c]
1	1	28	56
2	2	43	43
3	3	65	43.3
4	4	72	36
5	5	73	29.2

[a] Electrolytic conditions: 3-hexene-1,6-dioic acid (20 mmol), H_2SO_4 (40 mL, 1 mol L^{-1}), current density 8 mA cm^{-2} at 60 °C, Ni cathode and Pt anode.
[b] Isolated yield based on 3-hexene-1,6-dioic acid (20 mmol).
[c] Current efficiency.

For the electrochemical reduction, the temperature is an important factor. Table 5 shows the effect of temperature on the electroreduction of 3-hexene-1,6-dioic acid. Low temperature is not favorable for the electroreduction (Table 5, entries 1 and 2). The reason may be that the solubility of 3-hexene-1,6-dioic acid or product adipic acid in H_2O solvent is limited at low temperature. On the other hand, from the reaction kinetics of viewpoint, the increase of temperature can speed up the reaction rate. In the present electroreduction system, the reduction of 3-hexene-1,6-dioic acid is in competition with some other process, probably hydrogen evolution. Temperature will affect the kinetics of these competing processes. Increasing temperature may promote the reduction of 3-hexene-1,6-dioic acid. When electrolytic temperature changed from 40 to 60 °C, the yield of adipic acid increased from 48% to 65% (Table 5, entries 2 and 3). We noted that the yield did not improve (Table 5, entries 3-5) when electrolytic temperature increased from 60 to 80 °C. So the appropriate temperature for the electroreduction is 60 °C.

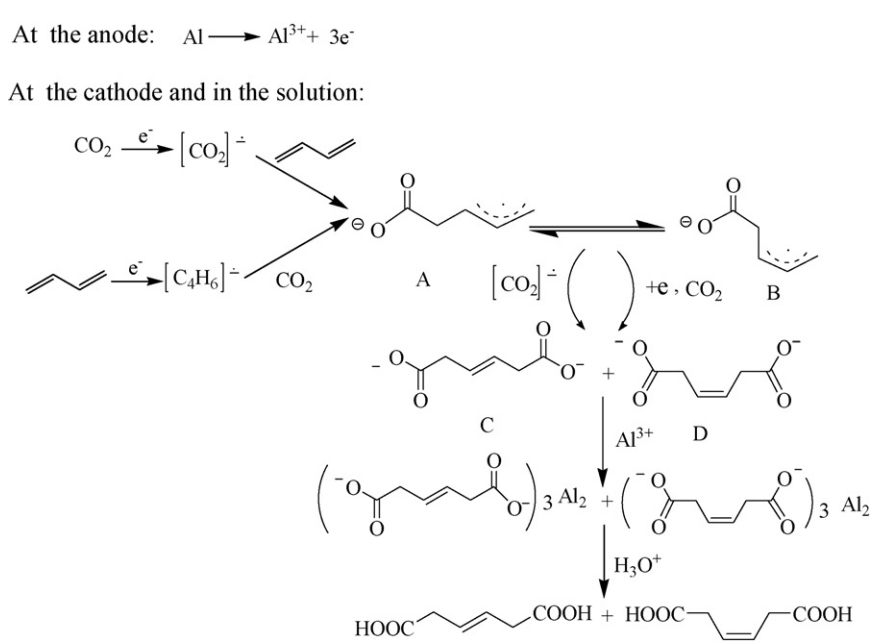
Electricity is another key factor for the electroreduction. The results obtained at different electricity are listed in Table 6. It can be seen that the yield of adipic acid increases from 28% to 73% upon increasing the charge consumption from 1 to 5 F mol^{-1} (Table 6, entries 1–5). However, the current efficiency gradually decreases. Taking the yield and the current efficiency into consideration, the electricity 3 F mol^{-1} is appropriate for the electroreduction of 3-hexene-1,6-dioic acid.

The above-mentioned experimental results indicate that the synthesis of adipic acid from CO_2 and 1,3-butadiene is feasible via the two-step electrochemical route. The present work provides a valuable synthetic route for adipic acid.

3.5. The reaction mechanism of 1,3-butadiene and CO_2

The electrochemical reaction mechanism of 1,3-butadiene and CO_2 has already been studied, however there have two different views. One view is the addition of $[CO_2^{\bullet}]^-$ radical anions produced from the reduction of CO_2 to butadiene [38]; the other is the allyl radical anions derived from the reduction of butadiene as nucleophiles to attack carbon dioxide [44–46]. We guessed that both cases actually existed at the same time. Namely, a competition reduction between 1,3-butadiene and CO_2 should be considered. In order to account for this hypothesis, the CV of 1,3-butadiene and CO_2 in a 0.07 mol L^{-1} n-Bu_4NBr-DMF solution (as shown in Fig. 3) was further investigated. It can be seen from Fig. 3 that the reduction current of 1,3-butadiene and CO_2 appeared almost at the same reduction potential. At the potential of −2.25 V versus SCE, the reduction current of 1,3-butadiene is quite obvious, as that of CO_2. Thus, it is reasonable to believe that the electrochemical reductions of CO_2 and 1,3-butadiene could occur almost at the same time under the same conditions.

According to our experimental results and the references [38,41,42,47], the plausible mechanism of 1,3-butadiene and CO_2 is proposed in Scheme 2. CO_2 is reduced into radical anion which



Scheme 2. Electrochemical reaction mechanism of 1,3-butadiene with CO_2.

attacks 1,3-butadiene to give intermediate A (carboxylate radical anion). At the same time, one-electron reduction of 1,3-butadiene generates allyl radical anion which reacts with CO_2 to afford A. A could be easily converted to B. Then, the coupling of A or B with CO_2 radical anion could give a dicarboxylate anion C and D. In addition, the reduction of the intermediates A and B, followed by nucleophilic attack of the ensuing carbanion on CO_2 could also generate C and D because the standard reduction potentials of allylic radicals [48] are more positive than that of CO_2 [49]. C and D combine with Al^{3+} ions to form stable aluminum carboxylates. The treatment of the metal carboxylates with acid gives dicarboxylic acids. For the electrodicarboxylation of other dienes with substituted groups with CO_2, only *trans* form dicarboxylic acids were obtained. This may be related to the steric hindrance effect among these groups in the products. Although the formation process of dicarboxylic acids is rather complicate, it can be seen that the products depend remarkably on the nature of the electrode material, which indicates that this process is electrocatalytic [37].

4. Conclusions

In summary, we have described a simple and efficient electrochemical method with Ni as the cathode under 3 MPa pressure of CO_2 using 1,3-diene and CO_2 as starting materials for the selective synthesis of 3-ene-1,6-dioic acid derivatives. Further, 3-hexene-1,6-dioic acid could be electrochemically reduced into an important industrial chemical adipic acid. The present electrochemical route possesses obvious advantages such as high regioselectivity, friendly environment, and usage of cheap and abundant raw materials. More importantly, the electrochemical route seems to be more promising in chemical industry due to the utilization of CO_2 and the ever-growing demand for adipic acid.

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