



Short communication

Selective monocarboxylation of olefins at $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ electride cathode



Jiang Li ^{a,*}, Shinsuke Inagi ^b, Toshio Fuchigami ^b, Hideo Hosono ^a, Setsuro Ito ^{a,c}

^a Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

^b Department of Electronic Chemistry, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

^c Research Center, Asahi Glass Co., Ltd., 1150 Hazawa-cho, Kanagawa-ku, Yokohama 221-8755, Japan

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ABSTRACT

Metallic oxide conductor $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (C12A7) electride with high affinity to CO_2 , a new candidate for the cathode material in electrochemistry, is used for the selective monocarboxylation of various olefins. The galvanostatic electrolysis was performed under carbon dioxide atmosphere without sacrificial anode in a divided cell. The monocarboxylic products were obtained in moderate to high yield (58–91%), which were significantly higher than those at Pt (9–83%) and glassy carbon (32–72%) cathode.

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1. Introduction

Fixation of carbon dioxide into organic substrates for preparing valuable chemicals is an attractive goal in organic synthesis. The electrochemical method is one of the efficient routes which was used for the fixation of CO_2 to various organic compounds, including benzylic halides [1–5], ketones [6–8], imines [9,10], and olefins [11–17]. Conventionally, electro-carboxylation was performed in an undivided cell with Mg or Al sacrificial anode. For instance, the carboxylation of phenyl-substituted alkenes to form 1,2-dicarboxylic acids was achieved using Pt cathode and Mg anode in high yields [11]. However, electrochemical synthesis of monocarboxylic products from olefins always gave low yields [12–17]. Usually benzylic halides have to be used as starting materials to form the monocarboxylic products [1–5], or the Fe and Ni based catalyst were necessary for the monocarboxylation [18,19]. Hence, a halide-free and metal catalyst-free process for the monocarboxylic compound synthesis is desirable from a viewpoint of green sustainable chemistry.

Recently we found that $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (C12A7) electride could be used as cathode for the electro-reduction of oxygen to superoxide ions, which was used for organic synthesis [20]. C12A7 electride is

a metallic conducting oxide with very low work function of 2.4 eV (comparable to metal potassium) and chemical inertness [21,22]. It was found that C12A7 electride is a good adsorbent and chemical activator of CO_2 [23]. The adsorbed CO_2 amount on C12A7 electride surface, which corresponds to that of surface electron concentration, is 2–3 times as large as that on glassy carbon (GC) surface [24]. Therefore, we expected that C12A7 electride cathode would be better for the carboxylation than other conventional electrodes. Here we report the highly efficient and selective carboxylation of olefins to form monocarboxylic products in a divided cell by using C12A7 electride cathode (hereafter denoted as C12A7:e⁻ electrode) without sacrificial anode.

2. Experimental

The preparation of C12A7 electride has been described in detailed previously [20,25,26]. Briefly, CaCO_3 and $\gamma\text{-Al}_2\text{O}_3$ powders with a molar ratio of 12:7 were reacted at 1300 °C for 12 h in air to form C12A7 oxide. The product was crushed in ethanol solvent by planetary milling to obtain the fine powder. The pellets formed by cold-isostatic pressing the above powder at 200 MPa were sintered at 1350 °C for 24 h in dry oxygen atmosphere. The resultant translucent pellets with a relative density of >95% were obtained. These pellets were sealed in an evacuated silica glass tube with titanium metal shots and heated at 1100 °C for 24 h to reduce C12A7 oxide and hence introduce electrons.

* Corresponding author.

E-mail address: j-li@lucid.msl.titech.ac.jp (J. Li).

After removing the surface TiO_x layer, the black C12A7 electrode with an electron concentration of about $1.4 \times 10^{21} \text{ cm}^{-3}$ was attained. It was cut into columns (about $15 \times 2 \times 2 \text{ mm}$ for cyclic voltammetry measurement) and plates (about $20 \times 10 \times 1 \text{ mm}$ for galvanostatic electrolysis). Each side of these samples was polished to be a mirror surface. Then the samples were sealed in an evacuated silica glass tube and annealed at $950 \text{ }^\circ\text{C}$ for 10 min to form active surfaces [27].

CV measurements in an undivided cell and galvanostatic electrolysis in an H type divided cell separated by a G4 sintered glass filter were conducted in a $0.1 \text{ M Bu}_4\text{NClO}_4\text{-CH}_3\text{CN}$ solution with the substrate concentration of 10 mM . For galvanostatic electrolysis, the volume for the catholyte and anolyte were both 16 ml , and the size for the exposed cathodes and Pt anode were $10 \times 10 \text{ mm}$. CO₂ was bubbled during electrolysis. The catholyte after reaction was esterified by adding 5 mole fold of iodoethane or iodomethane and stirred at room temperature for 24 h. The products extracted with diethyl ether were identified by ¹H NMR measurements with nitromethane as an internal standard to calculate the crude yields.

3. Results and discussions

The cathodic reactions of methyl cinnamate (**1a**) were performed by galvanostatic electrolysis with a current density of $5 \text{ mA}\cdot\text{cm}^{-2}$ using a C12A7:e⁻ electrode (Table 1). The products were dominantly α-carboxylic compound **2a**, with a few percent of α, β-dicarboxylic compound **4a** and saturated ester **5a**. Moreover, the β-carboxylic compound **3a** was not observed in present study, while it was obtained using electrosynthesis in single cell with Mg anode [16]. When $3 \times 96,485 \text{ C}\cdot\text{mol}^{-1}$ of electricity was passed, **2a** was obtained in 91% yield. For comparison, Pt and GC electrodes were also used as cathode for the reaction. When the passed charge was $3 \times 96,485 \text{ C}\cdot\text{mol}^{-1}$, the yield of **2a** was 82% at Pt electrode, which was little lower compared to C12A7:e⁻ electrode, while the yield at GC electrode was only 67%. As shown in Table 1, both yield and selectivity of **2a** in the present study

Table 1
Carboxylation of methyl cinnamate (**1a**) with CO₂ at different electrodes.

$$\text{Ph}-\text{HC}=\text{CH}-\text{COOCH}_3 \xrightarrow[\text{Divided cell}]{\begin{array}{l} 1) +e^-, +\text{CO}_2 \\ 2) \text{Etl, 24 hr} \\ 5 \text{ mA}\cdot\text{cm}^{-2} \end{array}} \begin{array}{l} \text{Ph}-\text{CH}_2-\text{CH}(\text{COOEt})-\text{COOCH}_3 \\ \text{Ph}-\text{CH}(\text{COOEt})-\text{CH}_2-\text{COOCH}_3 \\ \text{Ph}-\text{CH}(\text{COOEt})-\text{CH}(\text{COOEt})-\text{COOCH}_3 \\ \text{Ph}-\text{CH}_2-\text{CH}_2-\text{COOCH}_3 \end{array}$$

1a (10 mM) **2a** **3a** **4a** **5a**

Cathode	Charge passed $n \times 96,485 \text{ C}\cdot\text{mol}^{-1}$	Yields			
		2a	3a	4a	5a
C12A7:e ^{-a}	2	63%	0	3%	2%
Pt ^a	2	57%	0	3%	2%
GC ^a	2	50%	0	3%	3%
C12A7:e ^{-a}	3	91%	0	5%	3%
Pt ^a	3	82%	0	4%	3%
GC ^a	3	67%	0	5%	4%
Ti ^b	2.8	41%	10%	15%	0
Stainless steel ^c	2	35%	0	0	32%

^a Present results which performed in divided cell using CH₃CN as solvent.

^b Reported in Ref. [16] which performed in single cell using CH₃CN as solvent and Mg as a sacrificial anode.

^c Reported in Ref. [17] which performed in single cell using ionic liquid as solvent and Mg as a sacrificial anode.

Table 2
Carboxylation of various olefins with CO₂ at different electrodes.

$$\text{R}_1-\text{C}(\text{R}_2)=\text{C}(\text{R}_3) \xrightarrow[\text{Divided cell}]{\begin{array}{l} 1) +e^-, +\text{CO}_2 \\ 2) \text{Mel, 24 hr} \\ 5 \text{ mA}\cdot\text{cm}^{-2} \end{array}} \begin{array}{l} \text{R}_1-\text{C}(\text{R}_2)-\text{C}(\text{R}_3)-\text{COOMe} \\ \text{R}_1-\text{C}(\text{R}_2)-\text{C}(\text{R}_3)-\text{COOMe} \\ \text{R}_1-\text{C}(\text{R}_2)-\text{C}(\text{R}_3)-\text{COOMe} \\ \text{R}_1-\text{C}(\text{R}_2)-\text{C}(\text{R}_3)-\text{COOMe} \end{array}$$

1 (10 mM) **2** **4**

Substrate	R ₁	R ₂	R ₃
1b	Ph	H	Ph
1c	Ph	CH ₃	H
1d	H	Ph	CH ₃

Substrate	Cathode	E _{red, peak} ^a (V vs SCE)	Yields	
			2	4
1b	C12A7:e ⁻	-2.32	83%	8%
1b	Pt	-2.33	22%	2%
1b	GC	-2.35	60%	5%
1c	C12A7:e ⁻	-2.71	63%	5%
1c	Pt	-2.44	14%	2%
1c	GC	-2.75	47%	4%
1d	C12A7:e ⁻	-2.82	58%	6%
1d	Pt	-2.57	9%	1%
1d	GC	-2.88	32%	4%

^a The peak for the first reduction wave without the supply of CO₂.

were much higher than those obtained using sacrificial anode in a single cell [16,17].

To further check the activity of C12A7:e⁻ electrode, the same cathodic reduction was performed for various olefins, which are not substituted with electron-withdrawing group, and the results are summarized in Table 2. The dominant product was the monocarboxylic compound **2**, and C12A7:e⁻ electrode always gave the highest yield on **2** among present three electrodes for all substrates. Contrary to **1a**, the use of Pt cathode resulted in a low yield of **2b–2d**. For instance, the yields of **2b** are 83%, 22% and 60% for C12A7:e⁻, Pt and GC electrode, respectively.

To clarify the reduction characteristics at different electrodes, cyclic voltammetry measurement was performed by using SCE as reference electrode. At first, the CO₂ reduction at different electrodes was investigated for the CO₂ saturated $0.1 \text{ M Bu}_4\text{NClO}_4\text{-CH}_3\text{CN}$ solution. An intense CO₂ reduction which started at -1.9 V (curve a in Fig. 1) was observed at a Pt electrode. However, only a weak and broad reduction peak at around -2.6 V which is due to the reduction of CO₂ [13] was observed

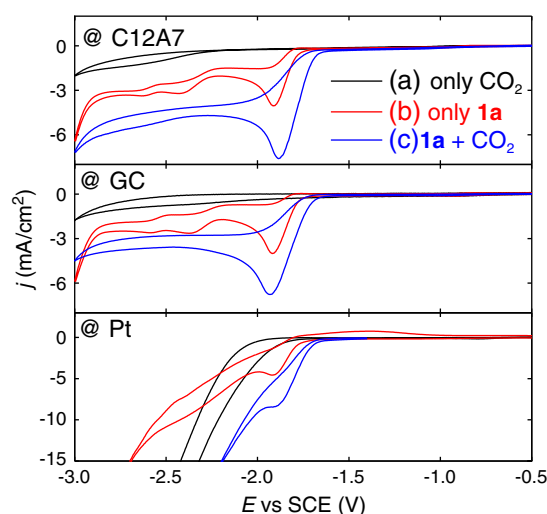


Fig. 1. Cyclic voltammograms in $0.1 \text{ M Bu}_4\text{NClO}_4\text{-CH}_3\text{CN}$ solution at different electrodes for (a) saturated CO₂, (b) 10 mM methyl cinnamate **1a** and (c) 10 mM **1a** with saturated CO₂. The sweep rate is $100 \text{ mV}\cdot\text{s}^{-1}$.

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