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Biomass-derived Cu/porous carbon for electrocatalytic synthesis of cyclic carbonates from CO_2 and diols under mild conditions

Jing-Jie Zhang, Shi-Ming Li, Yi Shi, Qiao-Li Hu, Huan Wang and Jia-Xing Lu**

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai, 200062, China. E-mail: hwang@chem.ecnu.edu.cn, jxlu@chem.ecnu.deu.cn; Tel: +86 21-52134935, +86 21-62233491

1 Chemicals and instruments

All reagents were commercially available (Aldrich) and were directly used without further purification.

Phase structures of the as-synthesized samples were characterized by X-ray diffraction (XRD) using Bruker D8 ADVANCE instrument using Cu-Kα radiation (λ = 1.5418 Å) at 35 kV and 25 mA.

Studies on surface chemistry was conducted by X-ray photoelectron spectroscopy (XPS) using an AXIS SUPRA^{TM}. Binding energies were calibrated using the containment carbon (C 1s = 284.6 eV).

The chemical compositions of PC and Cu/PC hybrids were determined with thermogravimetric analysis (TGA) measured by a Metzsch TGA-STA449F3 analyzer from 25 to 800ºC in an air flow of 50 mL min^{-1} at a heating rate of 10 ºC·min^{-1}.

The amounts of Cu in composite was quantified by Inductively Coupled Plasma-

Atomic Emission Spectrometry (ICP-AES) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer after dissolving the samples in HNO_3 solution and filtered.

The Scanning Electron Microscope (SEM) images were obtained on a Hitachi S-4800 field-emission scanning microscope.

The porous nature of the samples was investigated by the nitrogen adsorption-desorption isotherm at -196 ℃ recorded on a Quancachrome Autosorb-3B surface area and porosity analyzer. The specific surface area was calculated from the nitrogen adsorption isotherm within the relative pressure range of 0.04-0.20 by the Brunauer-Emmett-Teller (BET) method.

All electrochemical experiments were performed on a CHI 650 a electrochemical work station (Chenhua, Shanghai, China) in an undivided cell

The yield of products were quantified on an Shimadzu GC-2014 GC equipped with a flame ionization detector and a Rtx®-5 column (30 m × 0.25 mm × 0.25 μm) using biphenyl as an internal standard. The formula is as follows:

$f = (A_s / m_s) / (A_r / m_r)$

$mi = f \times A_i / (A_s / m_s)$

Among them, f stands for correction factor.

A_s and A_r represent the peak areas of the internal standard and the control respectively.

m_s and m_r are the amount of internal standard and control respectively.

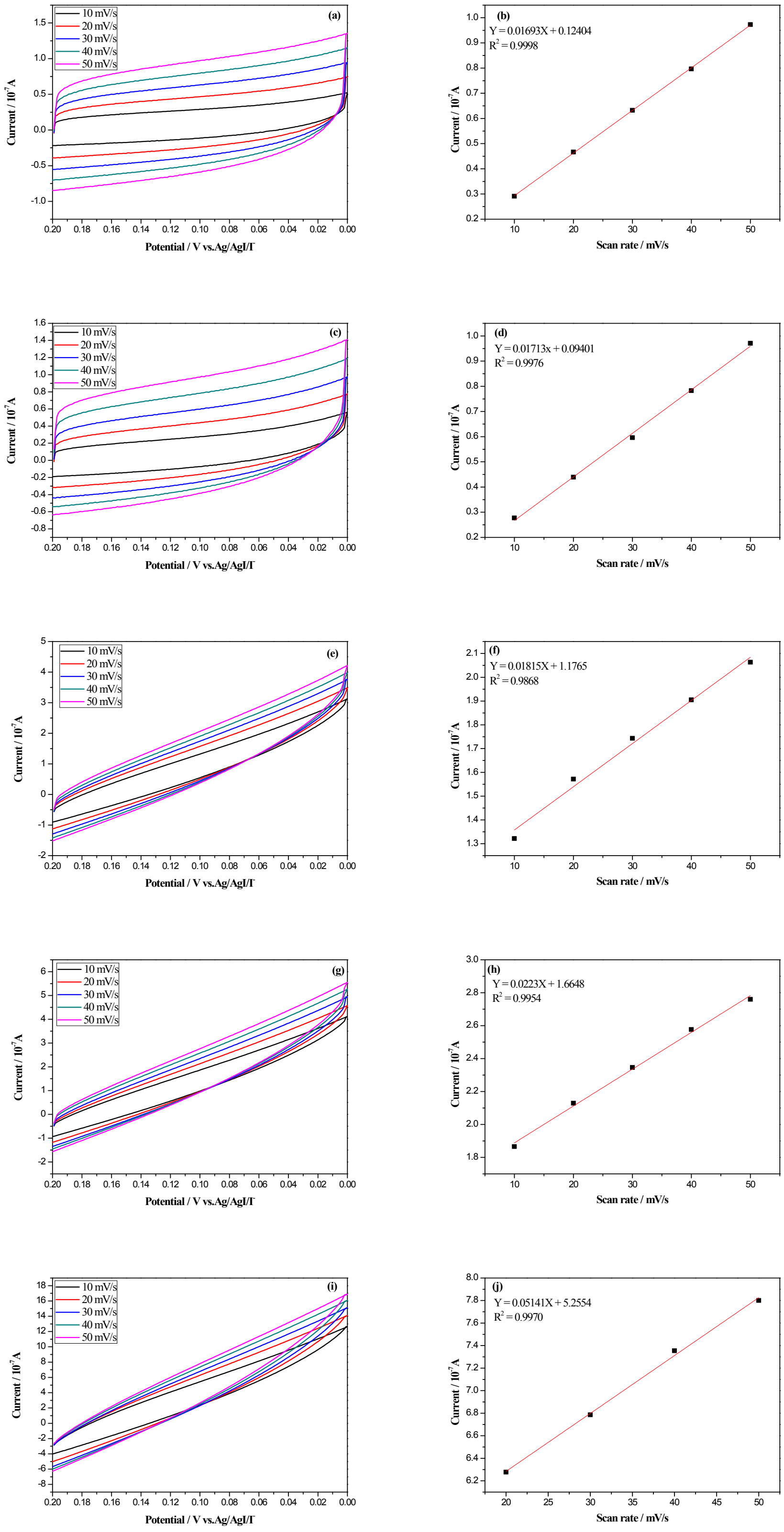
A_i is the peak area of the standard product.

M_i is the content of the target product.

2 The testing of the electrochemical active surface areas (ECSA)

The ECSA of the resulting composites are evaluated by cyclic voltammetry (CV). Cyclic voltammograms are measured with CHI600c electrochemical analyzer in a conventional three-electrode cell. The test conditions are as follows: porous carbon and Cu/PC composites are coated on the glassy carbon (GC) electrode which are used as working electrodes. $Ag/AgI/I^-$ is the reference electrode; platinum mesh is the counter electrode; the solution is acetonitrile containing 0.1 M tetraethylammonium iodide (TEAI). The double-layer capacitance (C_{dl}) was calculated according to the equation $I = C_{dl} / \upsilon$, (where I is the current at 0.1 V, and υ is the scan rate). The roughness factor (R_f) was determined by $R_f = C_{dl} / C_{dl}(GC)$ (where $C_{dl}(GC)$ is the C_{dl} of GC). The ECSA was calculated according to the equation $ECSA = R_f \times S$, where S was the area of GC ($S = 0.0314\ cm^2$ in this work) .

The ECSA of porous carbon and composites are explored by electric double layer capacitance method. Figure 1 (a, c, e, g, i, k) shows the cyclic voltammetry test in the range of 0.2 - 0 V, Figure 1 (b, d, f, h, j, l) is the linear plot of the reduction current versus scan rate. The C_{dl}, the roughness (R_f) relative to the glassy carbon and the ECSA of each material are listed in Table 1. It can be observed From Table1, the ECSA of GC, PC, Cu/PC- I, Cu/PC-II, Cu/PC-III, and Cu/PC-IV are 0.0314 cm^2, 0.0320 cm^2, 0.0366 cm^2, 0.0414 cm^2, 0.0951 cm^2 and 0.0515 cm^2 respectively. The ECSA of the composites are higher than that of porous carbon, suggested an increase in the number of electrochemically active sites with the addition of Cu. The ECSA of the composites first increases and then decreases, among them, Cu/PC-III reaches the maximum.


(a)
10 mV/s
20 mV/s
30 mV/s
40 mV/s
50 mV/s
Current / 10^{-7} A
Potential / V vs.Ag/AgI/I⁻
0.20 0.18 0.16 0.14 0.12 0.10 0.08 0.06 0.04 0.02 0.00
1.5 1.0 0.5 0.0 -0.5 -1.0
(b)
Y = 0.01693X + 0.12404
R^2 = 0.9998
Current / 10^{-7} A
Scan rate / mV/s
10 20 30 40 50
1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2
(c)
10 mV/s
20 mV/s
30 mV/s
40 mV/s
50 mV/s
Current / 10^{-7} A
Potential / V vs.Ag/AgI/I⁻
1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0 -0.2 -0.4 -0.6 -0.8
(d)
Y = 0.01713x + 0.09401
R^2 = 0.9976
Current / 10^{-7} A
Scan rate / mV/s
1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2
(e)
10 mV/s
20 mV/s
30 mV/s
40 mV/s
50 mV/s
Current / 10^{-7} A
Potential / V vs.Ag/AgI/I⁻
5 4 3 2 1 0 -1 -2
(f)
Y = 0.01815X + 1.1765
R^2 = 0.9868
Current / 10^{-7} A
Scan rate / mV/s
2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3
(g)
10 mV/s
20 mV/s
30 mV/s
40 mV/s
50 mV/s
Current / 10^{-7} A
Potential / V vs.Ag/AgI/I⁻
6 5 4 3 2 1 0 -1 -2
(h)
Y = 0.0223X + 1.6648
R^2 = 0.9954
Current / 10^{-7} A
Scan rate / mV/s
3.0 2.8 2.6 2.4 2.2 2.0 1.8
(i)
10 mV/s
20 mV/s
30 mV/s
40 mV/s
50 mV/s
Current / 10^{-7} A
Potential / V vs.Ag/AgI/I⁻
18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8
(j)
Y = 0.05141X + 5.2554
R^2 = 0.9970
Current / 10^{-7} A
Scan rate / mV/s
20 25 30 35 40 45 50
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2

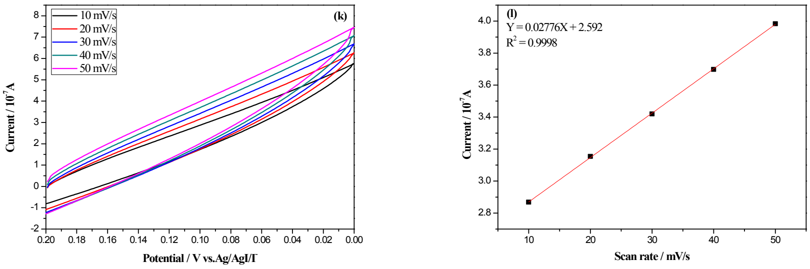


Fig. S1. CV curves (a, c, e, g, i, k) and plots of currents as a function of scan rate (b, d, f, h, j, l) of GC (a, b), PC (c, d), Cu/PC-I (e, f), Cu/PC-II (g, h), Cu/PC-III (i, j), and Cu/PC-IV (k, l) respectively in 0.1 M TEAI of CH_3CN at different scan rates

Table S1 ECSA date on different electrodes

Electrode	C_{dl}[a] (μF)	R_f[b]	ECSA[c] (cm^2)
GC	1.693	1	0.0314
PC	1.731	1.02	0.0320
Cu/PC- I	1.815	1.07	0.0336
Cu/PC-II	2.236	1.32	0.0414
Cu/PC-III	5.141	3.03	0.0951
Cu/PC-IV	2.776	1.64	0.0515

[a] double-layer capacitance(C_{dl}) was calculated according to the equation $I = C_{dl} / \upsilon$

[b] the roughness factor (R_c) was determined by the relative $R_f = C_{dl}/C_{dl}(GC)$ based on the cdl of a smooth surface (GC)

c the ECSA was calculated according to the equation ECSA = $R_f \times S$, where S was the area of GC (S = 0.0314 cm^2 in this work)

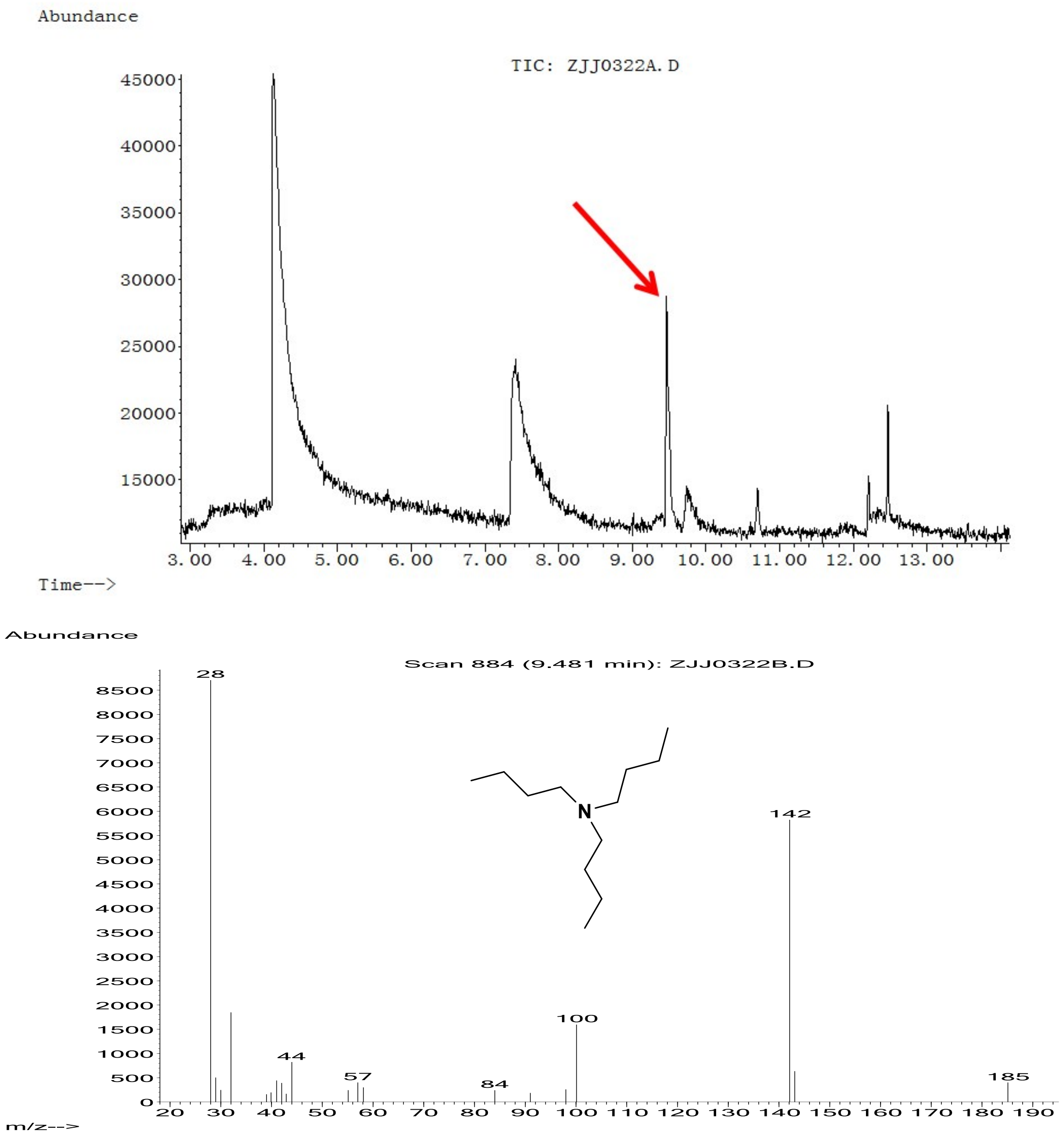


Fig. S2. The GC-MS figures of the Bu_3N.

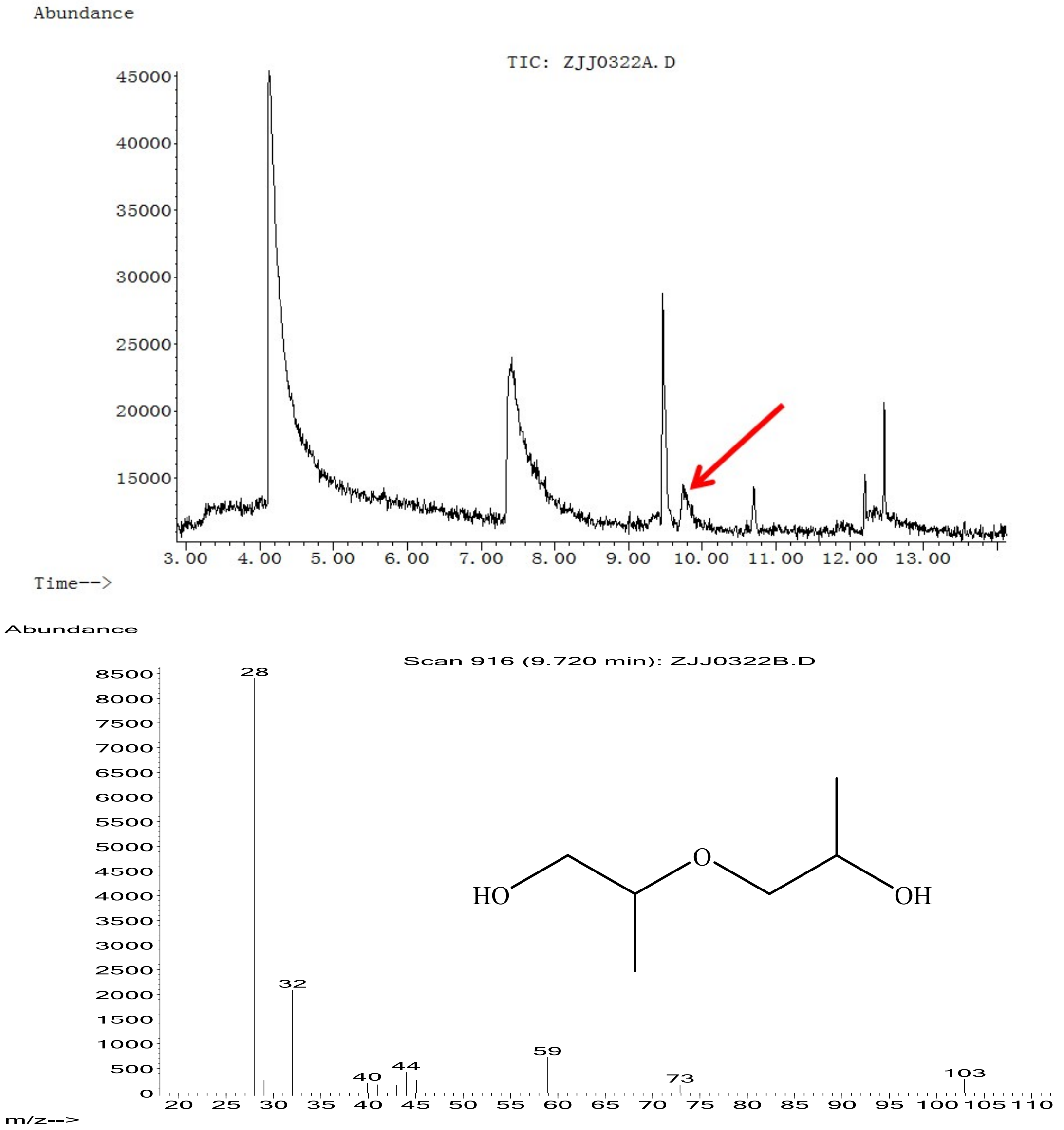


Fig. S3. The GC-MS figures of the dimerization product.

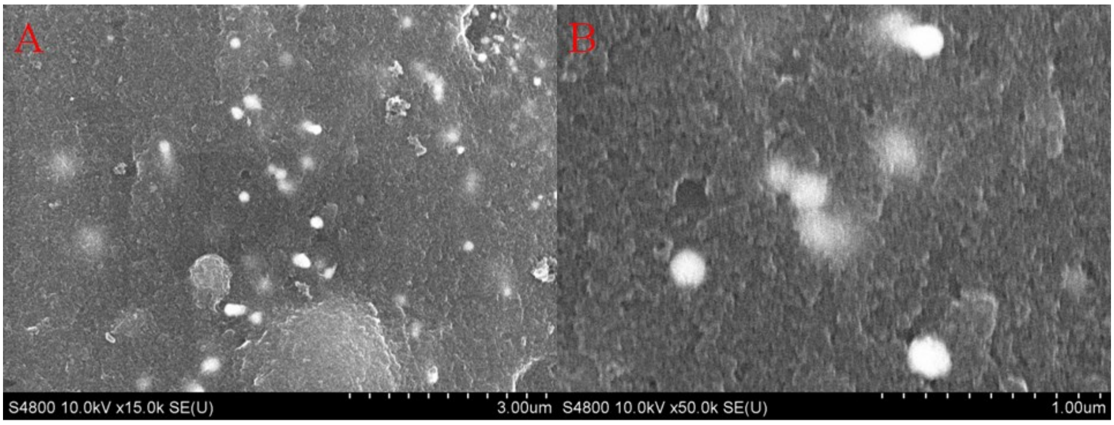


Fig.S4. SEM images of Cu/PC-III after use at different magnifications (A: 15k, B: 50k).

Table S2. Comparison of the yield of propylene carbonate from CO_2 and diol with other references.

Cathode	Electrolyte	Electrochemical cell	Electrolysis condition	diols	Yield (%)	Ref.
Cu/PC-III	MeCN-0.1 M TEAI	Divided cell	j = 12.25 mA/cm^2, T = r.t.	1b	46.3	This work
Cu/PC-III	MeCN-0.1 M TEAI	Divided cell	j = 12.25 mA/cm^2, T = r.t.	1e	37.9	This work
Cu	MeCN-0.1 M TEAI	Divided cell	j = 17.25 mA/cm^2, T = 0 ^{o}C	1b	19	1
Ni	BMIMBF$_4$	Undivided cell	E = -1.7 V, T = 50 ^{o}C	1b	4	2
Cu	MeCN-0.1 M TBAI	Undivided cell	j = 4.14 mA/cm^2, T = 25 ^{o}C	1b	21	3
Pt	MeCN-0.1 M TEAP		j = 5 mA/cm^2, T = 0 ^{o}C	1e	28	4

References:

[1] H. Wang, L.-X. Wu, J.-Q. Zhao, R.-N. Li, A.-J. Zhang, H. Kajiura, Y.-M. Li and J.-X. Lu, *Greenh. Gases*, 2012, **2**, 59-65.

[2] H. Wang, L.-X. Wu, Y.-C. Lan, J.-Q. Zhao and J.-X. Lu, *Int. J. Electrochem. Sci.*, 2011, **6**, 4218-4227.

[3] L.-X. Wu, H. Wang, L. He, L. Wu, A.-J. Zhang, H. Kajiura, Y.-M. Li and J.-X. Lu, *Int. J. Electrochem. Sci.*, 2012, **7**, 5616-5625.

[4] Casadei, M. A.; Cesa, S.; Rossi, L., Electrogenerated base-promoted synthesis of organic carbonates from alcohols and carbon dioxide. *Eur. J. Org. Chem.* **2000,** (13), 2445-2448.