

## Supporting Information

# Microbubble effect-assisted electrolytic synthesis of hollow carbon spheres from CO<sub>2</sub>

*Bowen Deng, Xuhui Mao<sup>\*</sup>, Wei Xiao, Dihua Wang<sup>\*</sup>*

School of Resource and Environmental Sciences, Hubei International Scientific and Technological Cooperation Base of Sustainable Resource and Energy, Wuhan University, 430079 Wuhan, China

## **Text S1 Experimental Section**

### **Electrochemical analysis of melts**

Anhydrous LiCl, KCl and CaCO<sub>3</sub> with analytical purity were purchased from Sinopharm Chemical Reagent Co. Ltd. The indirect electrochemical reduction of CO<sub>2</sub> was conducted in molten eutectic mixture of LiCl–KCl (58.5:41.5 molar ratio) containing 2 mol% CaCO<sub>3</sub>. The operating temperature of the CaCO<sub>3</sub>-containing LiCl-KCl molten salts was 450 °C. The experimental setup was reported in our previous works.<sup>1-2</sup> Approximately 500 g salts were added to an alumina crucible and were dried at 300 °C under argon for 24 h to remove the moisture before being heated up to the target temperature.

The electrochemical behaviors of the LiCl–KCl eutectic mixture with or without 2 mol% CaCO<sub>3</sub> were investigated under argon and CO<sub>2</sub> atmospheres, respectively. Cyclic voltammetry (CV) measurements were performed on an electrochemical workstation (CHI-1140, CH Instrument Co. Ltd., USA) using a three-electrode system. The working electrode and the counter electrode were a nickel (Ni) wire (0.64 cm<sup>2</sup> in the electrolyte) and a graphite rod (4.00 cm<sup>2</sup> in the electrolyte), respectively. The reference electrode consisted of a silver wire placed in an alumina tube filled with 0.5 mol% AgCl-containing LiCl–KCl.

Potentiostatic electrolysis under various potentials were carried out in 2 mol % CaCO<sub>3</sub>-containing LiCl–KCl at 450 °C under argon atmosphere. A Ni sheet (3.00 cm<sup>2</sup> in the electrolyte) and graphite rod (4.00 cm<sup>2</sup> in the electrolyte) served as working electrode

and counter electrode, respectively. Over the electrolysis, the cell voltage between Ni sheet and graphite rod was monitored by a computer-controlled power source (Shenzhen Neware Electronic Co. Ltd., China).

### **Preparation of Hollow Carbon Spheres by constant-voltage electrolysis**

The synthesis process of hollow carbon spheres was performed by constant-voltage electrolysis in 2 mol % CaCO<sub>3</sub>-containing LiCl–KCl at 450 °C for 1 h using a computer-controlled power source (Shenzhen Neware Electronic Co. Ltd., China). The cathode and anode were a Ni sheet (3.00 cm<sup>2</sup> in the electrolyte) and a graphite rod (4.00 cm<sup>2</sup> in the electrolyte), respectively. CO<sub>2</sub> was continuously bubbled into the melt through an alumina tube during the constant-voltage electrolysis. Products deposited on the cathode were collected and rinsed with 1 M HCl and distilled water to remove the adherent frozen electrolyte, and were dried in a vacuum oven at 80 °C for 12 h.

### **Characterization of Hollow Carbon Spheres**

The obtained products were characterized by scanning electron microscopy (SEM, FEI Sirion field emission), Transmission Electron Microscopy (TEM, JEOL Ltd., JEM–2100, Japan), Energy Dispersive X–Ray Spectroscopy (EDX, EDAX Ltd., GENESIS XM2, USA), X–ray diffraction spectroscopy (XRD, Shimadzu X–ray 6000 with Cu K $\alpha$  radiation at 40 kV and 250 mA,  $\lambda$ =0.154 nm, Japan), Laser Confocal Raman Microspectroscopy (Renishaw RM1000, UK) at room temperature with an excitation

wavelength at 514.5 nm from a diode pumped solid-state laser and a Micromeritics ASAP 2020 (USA) automatic analyser at liquid N<sub>2</sub> temperature.

### **Electrochemical Measurements of Hollow Carbon Spheres**

The capacitive performance of carbon samples was investigated in 6 M KOH with a two-electrode testing cell. The electrodes were prepared into carbon films by mixing the carbon with polytetrafluoroethylene (PTFE) and commercial acetylene black (8: 1: 1). Nickel foam was used as a current collector and was covered by the carbon film with a surface area of about 0.8 cm<sup>2</sup>. The mass loading of the active material was approximately 5 mg cm<sup>-2</sup>. Two electrodes with almost identical mass loading were assembled in a cell for the measurements. CV, electrochemical impedance spectroscopy (EIS) and galvanostatic charge-discharge measurements were carried out on a PGSTAT 302N Autolab Electrochemical Workstation. The gravimetric capacitances C<sub>g</sub> (F g<sup>-1</sup>) were then calculated from the measured capacitance and the mass of active material using the equation displayed below:

$$C_g = \frac{2it}{\Delta V} \text{ (two-electrode testing cell)}$$

where *i* (A g<sup>-1</sup>) and *t* (s) represent the current density and discharge time in galvanostatic charge-discharge test, respectively, and Δ*V* (V) is the ohmic drop during the galvanostatic charge-discharge test (1 V in this study).

### **Thermodynamic Calculations for Electrochemical Reactions**

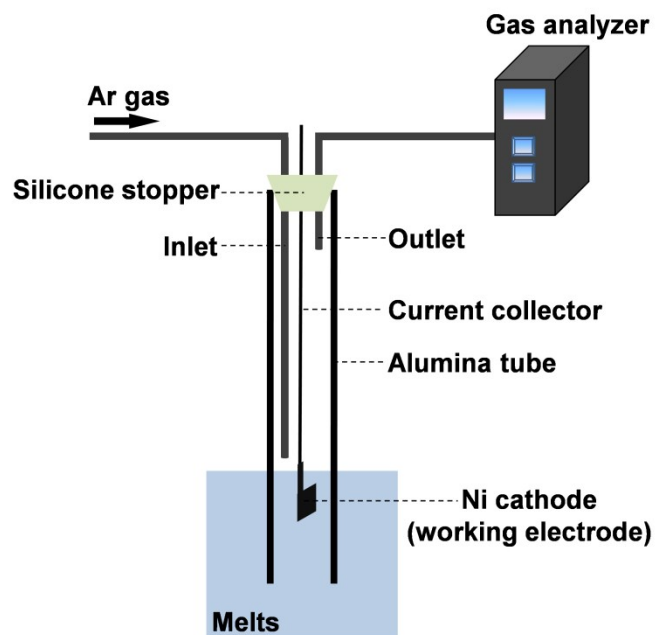
The theoretical decomposition cell voltage was calculated by following thermodynamic equation:

$$E = \frac{\Delta G}{nF}$$

where E (V) represents the theoretical decomposition voltage, and  $\Delta G$  ( $\text{kJ mol}^{-1}$ ) is Gibbs free energy change of reaction. All data used for calculation were obtained from HSC 5.1 software. F ( $\text{C mol}^{-1}$ ) is the Faraday constant, and n (mol) stands for the number of transferred electrons for each mole of reactant.

### **CO Gas Analysis**

In order to analyze the gas product, the electrolysis was conducted in a sealed alumina vessel (3 cm in diameter, 50 cm in length), which was immersed into melts with 5 cm depth (see Scheme S1 below). The Ni sheet (cathode) was placed inside the alumina vessel, and the depth of cathode immersed into the melts was merely 1.5 cm to ensure that the gaseous products on cathode can be completely collected from the vessel. The top of the alumina tube was bunged up with a silicone stopper which had an inlet and an outlet tube. Argon gas was aerated into the alumina inlet tube with a flow rate of  $1 \text{ L min}^{-1}$ . Gas analyzer (JH701, Jinghui Tech Co. Ltd., China) connected with the outlet tube was used for determining the gaseous products escaped from the vessel during potentiostatic electrolysis. The sampling flow rate of the gas analyzer was also  $1 \text{ L min}^{-1}$ . The schematic of the setup is shown as below:



Scheme S1. The setup for the detection of gaseous products during electrolysis.

Table S1. Gibbs free energy changes of possible electrochemical reactions.

Reactions	Temperature (°C)				
	350	450	550	650	750
	$\Delta G$ (kJ/mol)				
$2\text{KCl}=2\text{K}+\text{Cl}_2(\text{g})$	754.0	734.8	715.9	697.2	678.9
$2\text{LiCl}=2\text{Li}+\text{Cl}_2(\text{g})$	714.4	697.8	681.6	667.4	656.3
$2\text{CaO}=2\text{Ca}+\text{O}_2(\text{g})$	1138.8	1118.2	1097.5	1076.7	1055.9
$2\text{CaCO}_3=\text{CaC}_2+\text{CaO}+2.5\text{O}_2(\text{g})$	1446.2	1402.9	1359.2	1315.9	1272.9
$2\text{CaCO}_3=2\text{CaO}+2\text{CO}(\text{g})+\text{O}_2(\text{g})$	616.1	568.0	520.3	473.1	426.3
$\text{CaCO}_3=\text{CaO}+\text{C}+\text{O}_2(\text{g})$	474.6	459.6	444.7	430.0	415.5

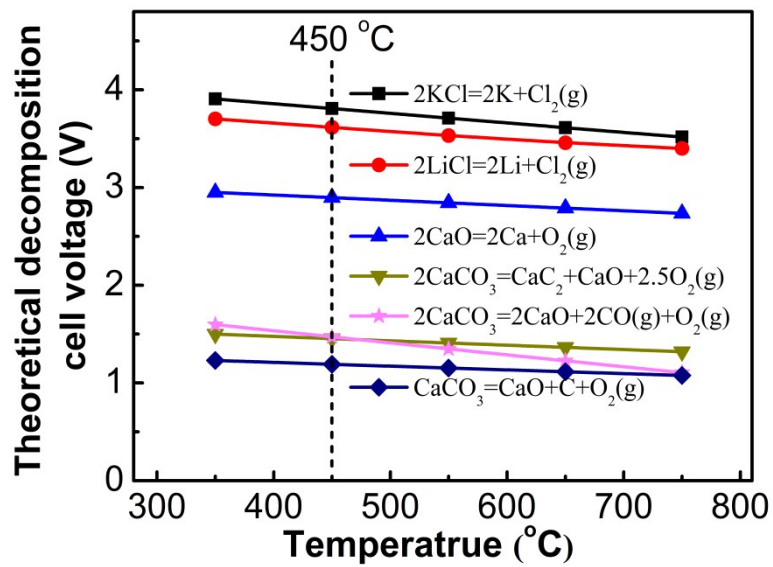


Figure S1. The theoretical decomposition cell voltages of possible electrochemical reactions in  $\text{CaCO}_3$ -containing molten  $\text{LiCl-KCl}$  under different temperatures.

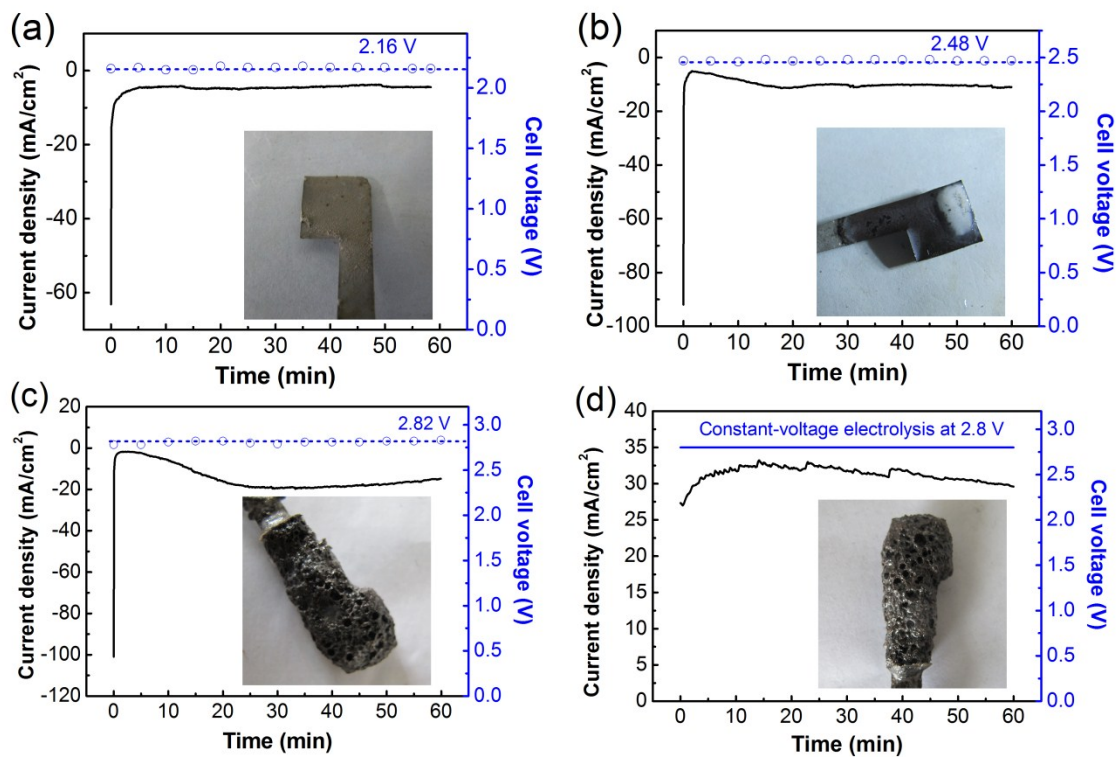


Figure S2. Current–time (*i*–*t*) curves and real-time monitored cell voltages under Ar atmosphere by potentiostatic electrolysis at (a) –1.2 V, (b) –1.5 V and (c) –1.8 V vs. Ag/AgCl. (d) Current–time (*i*–*t*) curves and real-time monitored cell voltages by constant-voltage electrolysis at 2.8 V with CO<sub>2</sub> bubbled into the melts. Insets: corresponding optical images of Ni electrodes after electrolysis without any post-treatment.



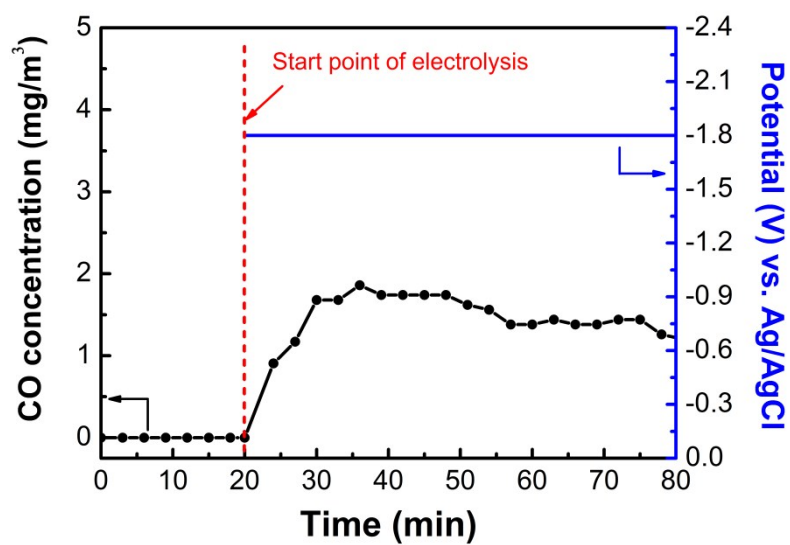


Figure S3. Profile of the detected CO during potentiostatic electrolysis at  $-1.8$  V vs. Ag/AgCl.

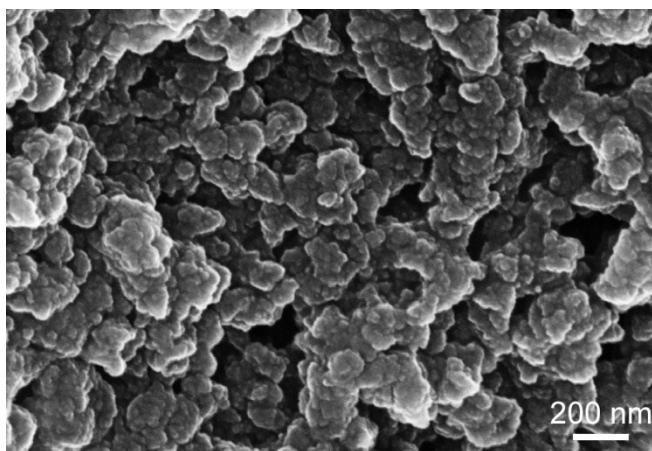


Figure S4. SEM image of carbon film obtained at  $-1.5$  V by potentiostatic electrolysis.

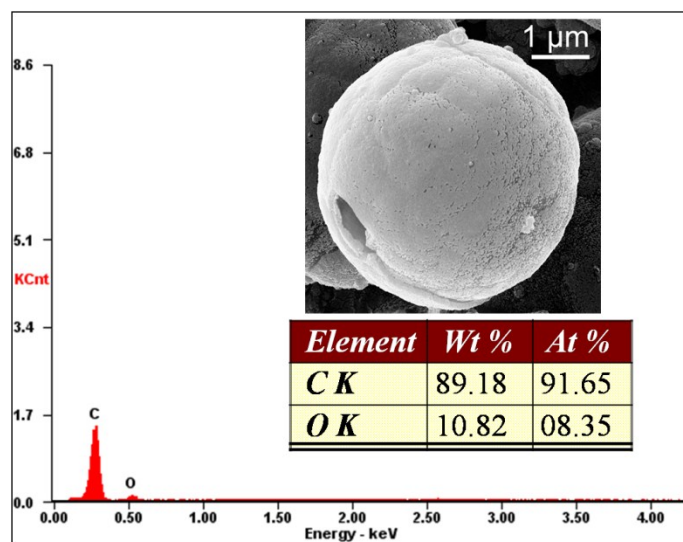


Figure S5. EDX result of hollow carbon spheres obtained after 2.8 V constant-voltage electrolysis. Inset: SEM image of hollow carbon spheres.

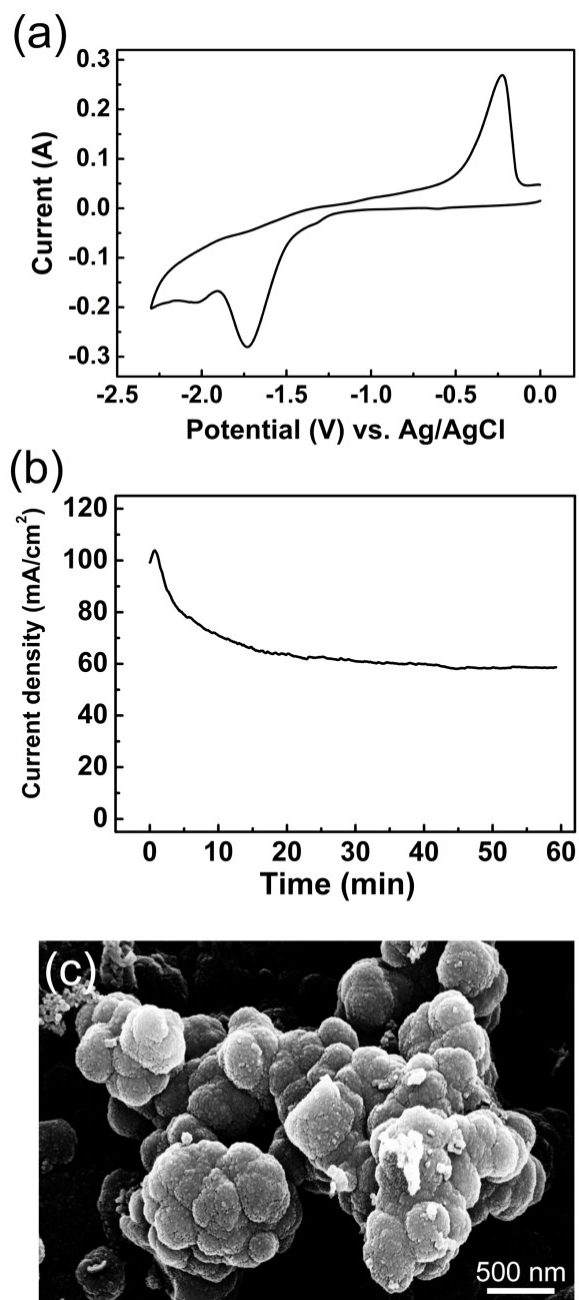


Figure S6. (a) Cyclic voltammetry in 2 mol%  $\text{Li}_2\text{CO}_3$ -containing  $\text{LiCl-KCl}$  at 450 °C. (b) Current-time (I-t) curve by constant-voltage electrolysis at 2.8 V in 2 mol%  $\text{Li}_2\text{CO}_3$ -containing  $\text{LiCl-KCl}$  at 450 °C. (c) SEM image of carbon obtained under constant-voltage electrolysis of 2.8 V at 450 °C (in  $\text{Li}_2\text{CO}_3$ -containing  $\text{LiCl-KCl}$ ).

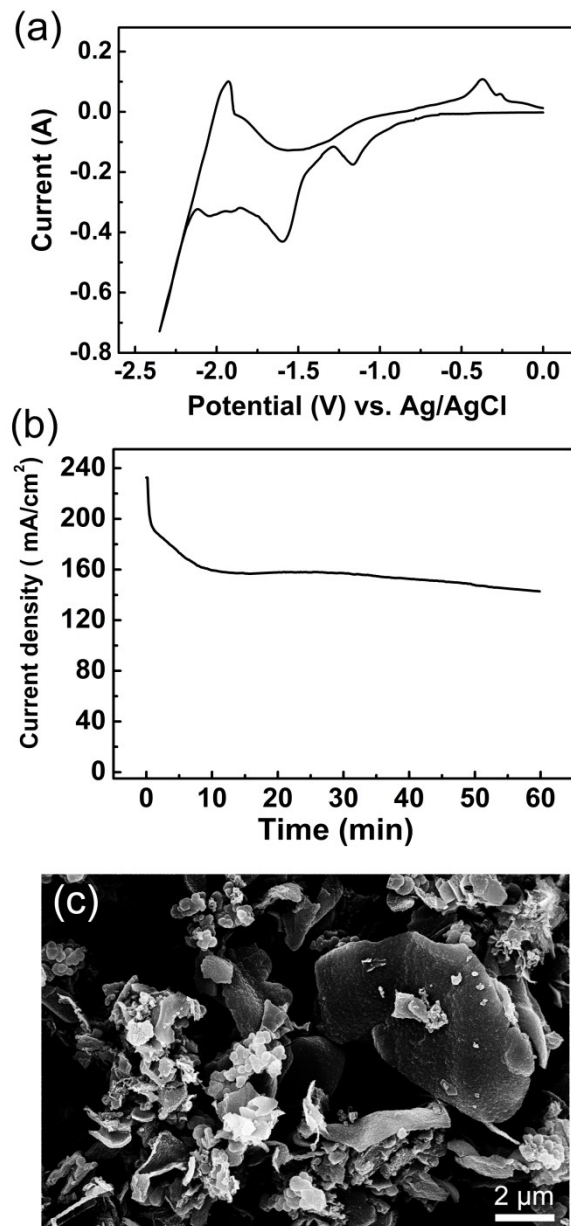


Figure S7. (a) Cyclic voltammetry in 2 mol% CaCO<sub>3</sub>-containing LiCl-KCl at 650 °C. (b) Current-time (I-t) curve by constant-voltage electrolysis at 2.8 V in 2 mol% CaCO<sub>3</sub>-containing LiCl-KCl at 650 °C. (c) SEM image of carbon obtained under constant-voltage electrolysis of 2.8 V at 650 °C (CaCO<sub>3</sub>-containing LiCl-KCl).

## References

- (1) Tang, D. Y.; Yin, H. Y.; Mao, X. H.; Xiao, W.; Wang, D. H. Effects of Applied Voltage and Temperature on the Electrochemical Production of Carbon Powders from CO<sub>2</sub> in Molten Salt with an Inert Anode. *Electrochim. Acta* **2013**, *114*, 567–573.
- (2) Yin, H. Y.; Mao, X. H.; Tang, D. Y.; Xiao, W.; Xing, L. R.; Zhu, H.; Wang, D. H.; Sadoway, D. R. Capture and Electrochemical Conversion of CO<sub>2</sub> to Value-Added Carbon and Oxygen by Molten Salt Electrolysis. *Energy Environ. Sci.* **2013**, *6*, 1538–1545.