

## Supplementary Information

### **A dissolved inorganic carbon measurement method featured self-calibration function via an electrodialytic generator**

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## **Reagents and materials.**

Unless otherwise stated, ultra-pure water (Milli-Q, USA) with a specific resistivity at 18.2 M $\Omega$ ·cm was used to prepare solutions. 1 M H<sub>2</sub>SO<sub>4</sub> and 1 M H<sub>3</sub>PO<sub>4</sub> standard solution, obtained from Aladdin Corp, Shanghai, China, were used to be diluted to the final acidic donor stream. Analyte solutions were prepared in the form of either sodium or potassium salts. Typically, these were analytical grade chemicals, used as received from the manufacturer.

## **Fabrication procedure of the cEDG**

Since high pressure tolerance range is not required for the present use, a stack of three layers of cation exchange membranes (CEMs) and a stack of three layers of anion exchange membranes (AEMs) are used to isolate the central eluent channel from two regenerant chambers outside, respectively. The CEMs side is at anode with respect to the cathode of AEMs side. A programmable control constant current source is connected with both electrodes. The eluent channel is packed by cation exchange resin (CER), which is aimed to reduce the resistance and the void volume of central channel as well. 1 M KHCO<sub>3</sub> solution is used as feed solution driven by a peristaltic pump (BT200, Lead Fluid Technology Corp., Longer Precision Pump Corp. China, [www.longerpump.com.cn](http://www.longerpump.com.cn)) flows through both regenerant chambers in one direction at the flow rate of 1 mL/min and pure water driven by a piston pump (Qingbohua Corp. China, [www.prehplc.com](http://www.prehplc.com)) flows through the eluent channel in the opposite direction to feed solution. Under the electric field, the electrolysis of water occurs at both electrodes of the device, and the H<sup>+</sup> ions generated at the anode and OH<sup>-</sup> ions generated at the cathode will displace K<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> in the feed solution, respectively. The displaced K<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> migrate across CEM and AEM into the central channel, respectively, to form a KHCO<sub>3</sub> solution. Such process follows the Faradaic law and the produced KHCO<sub>3</sub> solution is determined by the applied current and the flow rate of the water through the central channel. When the flow rate of the water is kept constant, a given concentration of KHCO<sub>3</sub> solution can be produced by controlling the applied current, offering standard carbon sample for calibration of DIC system. Fig.

S1 illustrates its configuration and the photograph of real device.

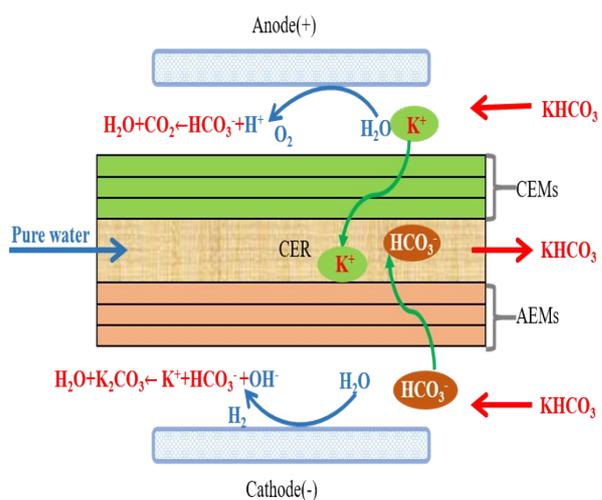
Note, the effective species of potassium bicarbonate or sodium bicarbonate for production of standard carbon solution are bicarbonate ions, potassium or sodium is only counterions. Here potassium bicarbonate other than sodium bicarbonate typically used in previous DIC systems was selected to be standard carbon solution, and the reason is  $K^+$  has the higher ionic mobility and thus leads to the lower voltage drop and lower Joule heating across the generator membrane.

#### **Calibration of bicarbonate solution.**

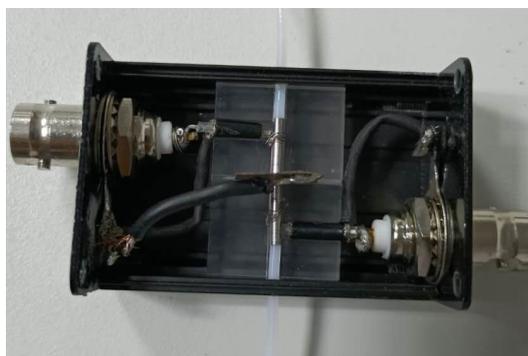
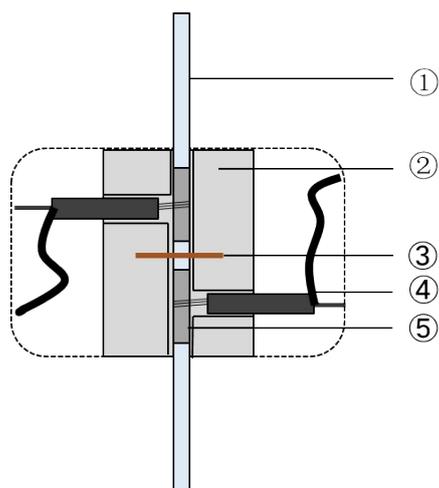
Since bicarbonate is a weak base and the fractions of concomitant anions (carbonate and hydroxide ions) vary in different concentration of bicarbonate solution. Here, the concentration calibration of bicarbonate solution was performed by a suppressed IC method, in which either carbonate or bicarbonate can be normalized to be carbonic acid followed by measuring its conductance to establish the calibration curve of conductance and concentration.<sup>27</sup>

#### **Sample preparation.**

The mineral water was purchased from local market and the tap water was collected in the lab. The river water was from Qingchun river near the campus, located in Shanghai. The simulated sea water was prepared by the standard criterion (DB44/T 475-2008) of China.

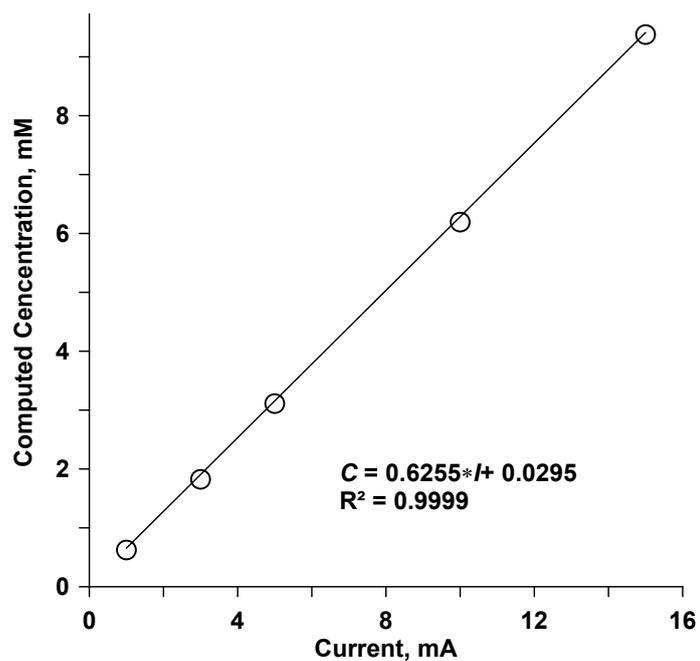


**Fig. S1.** Configuration of cEDG (left) and the photograph of real device (right)

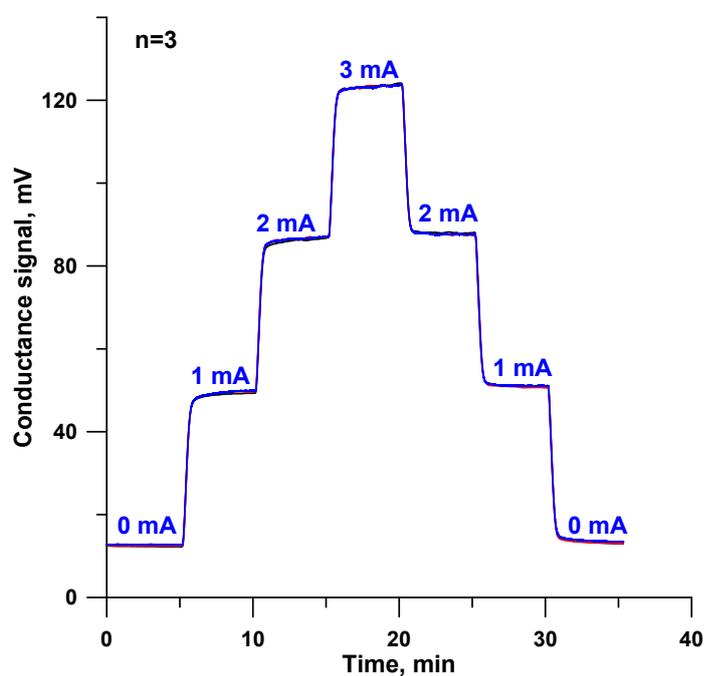


**Fig. S2.** Schematic diagram of C<sup>4</sup>D (left) and the photograph of detection cell (right)

- ① PTFE tubing; ② PMMA plate; ③ copper foil; ④ wire lead; ⑤ SS electrode.

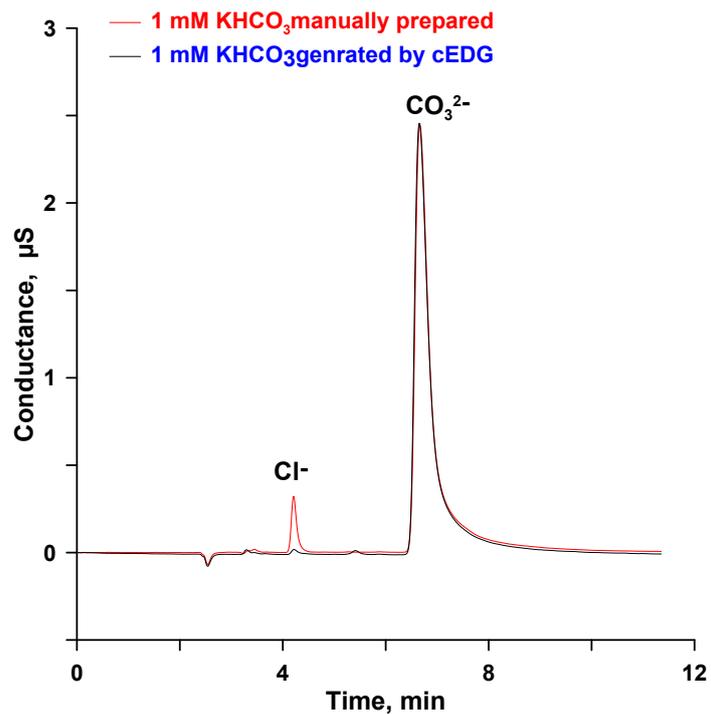


**Fig. S3.** Correlation of the applied current and the generated  $\text{KHCO}_3$  concentration at the flow rate of 1 mL/min.

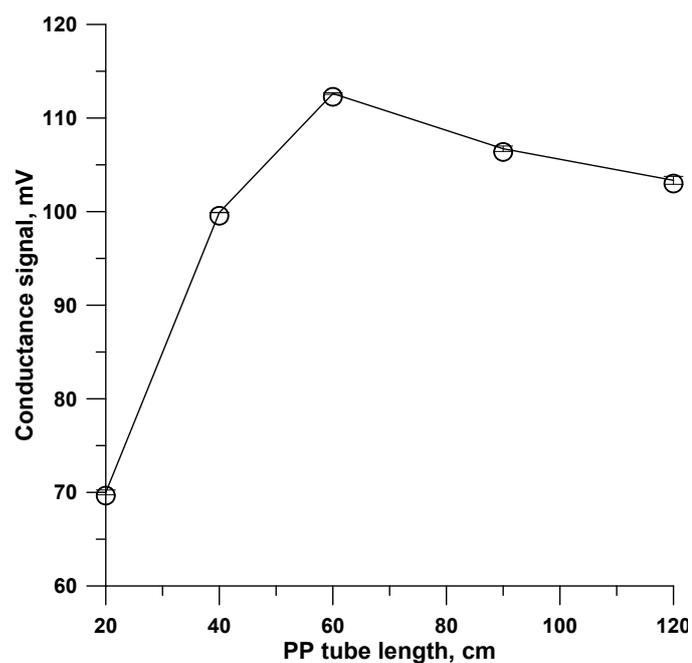


**Fig. S4.** Rise/fall curve of the cEDG.

Conditions: flow rate of pure water, 1 mL/min; step current varied at  $5 \cdot n$  ( $n=1, 2, 3, 4, 5, 6$ ) min.

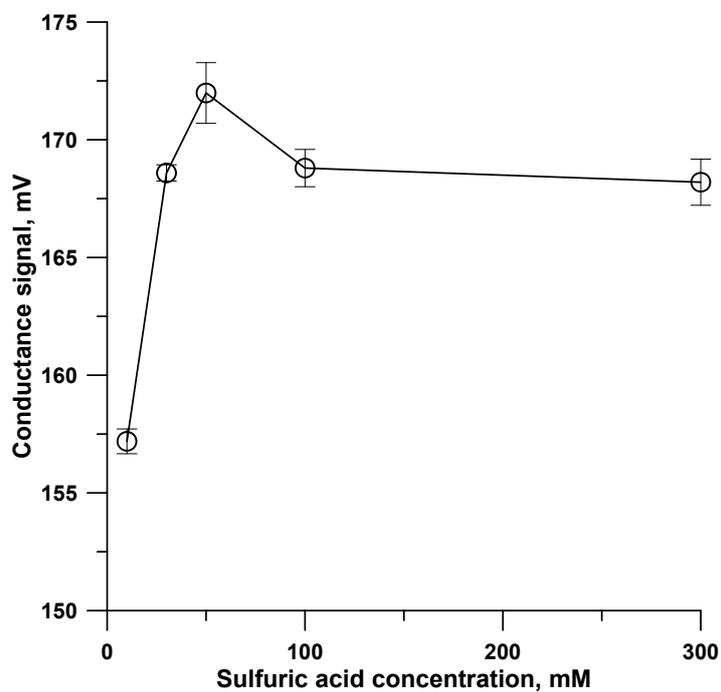


**Fig. S5.** Purity test of  $\text{KHCO}_3$  samples generated by cEDG and manually prepared  
Conditions: IC system, Dionex IC 2000; eluent, 10 mM KOH; suppression current, 25 mA; flow  
rate of eluent, 1 mL/min; column: AS20 (4.0 mm i.d.  $\times$  250 mm length); column temperature,  
30°C; sample, 1 mM  $\text{KHCO}_3$  (generated by cEDG or manually prepared); injection volume, 25  $\mu\text{L}$ .



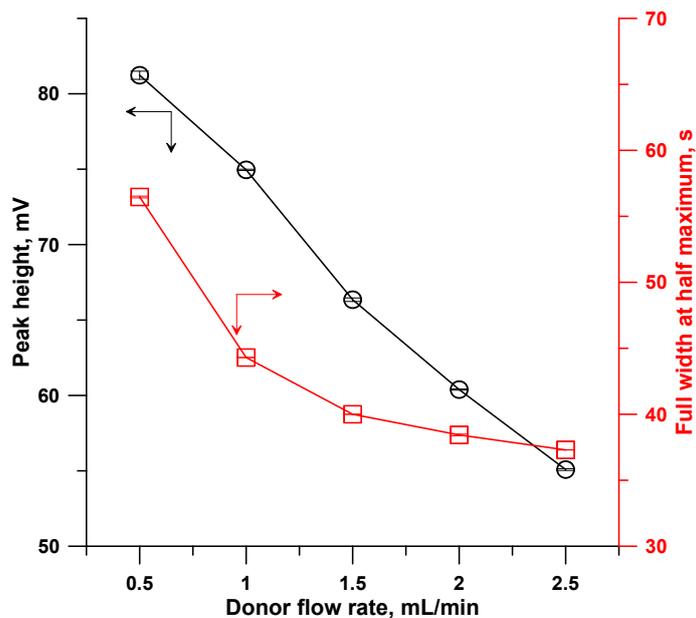
**Fig. S6.** Effect of length on the DIC response

Conditions, sample, 2 mM  $\text{KHCO}_3$ ; injection volume, 100  $\mu\text{L}$ ; concentration of sulfuric acid, 50 mM; flow rate of sulfuric acid donor stream and pure water acceptor stream, 1 mL/min.



**Fig. S7.** Effect of sulfuric acid concentration on the response

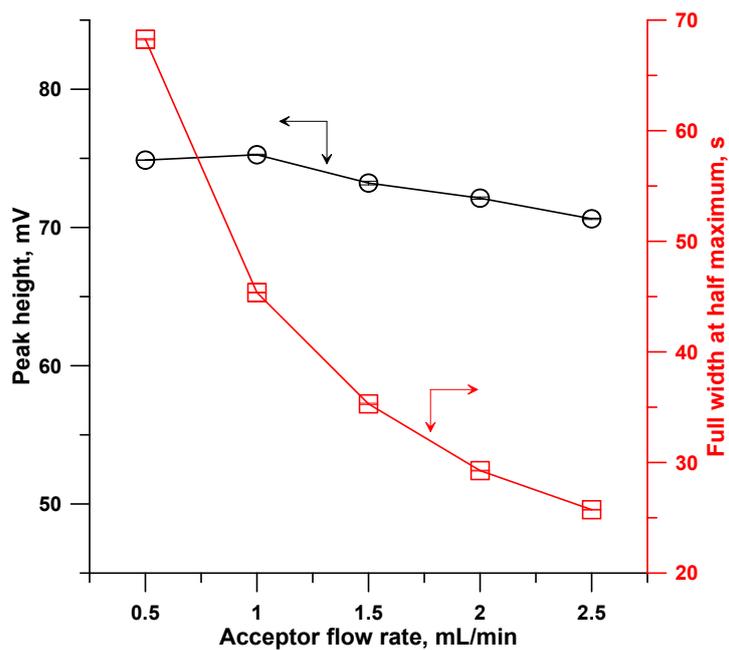
Conditions: sample, 5 mM  $\text{KHCO}_3$ ; Injection volume, 400  $\mu\text{L}$ ; flow rate of sulfuric acid, 1 mL/min; flow rate of pure water acceptor stream, 1 mL/min.



**Fig. S8.** Effect of flow rate of sulfuric acid solution

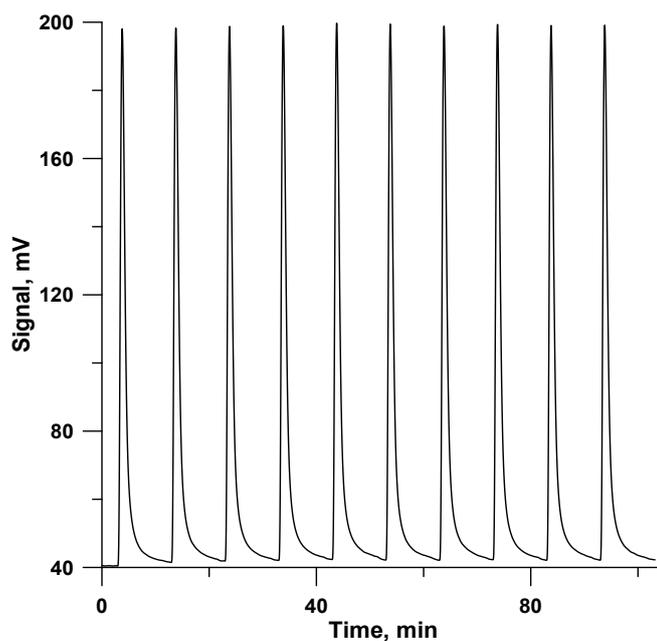
Conditions: sample, 2 mM  $\text{KHCO}_3$ ; Injection volume, 100  $\mu\text{L}$ ; sulfuric acid concentration, 50 mM;

flow rate of pure water acceptor stream, 1 mL/min.



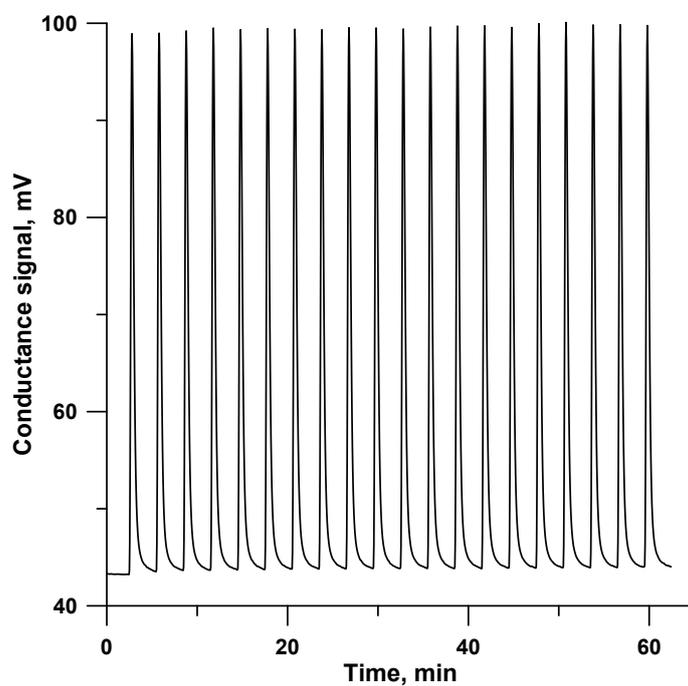
**Fig. S9.** Effect of flow rate of the acceptor stream of pure water

Conditions: flow rate of sulfuric acid stream, 1 mL/min; other conditions same as Fig. S6.



**Fig. S10.** The response of DIC analyzer to the samples generated by cEDG operated at constant current.

Conditions: current applied for cEDG, 3 mA; injection volume, 400  $\mu$ L.



**Fig. S12.** Throughput of the DIC analyzer at 20 consecutive injections.

Conditions, current applied for cEDG, 2.8 mA; flow rate of sulfuric acid donor stream and pure water acceptor stream, 2.5 mL/min; other conditions same as Fig. S10.