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An All-Solid-State Carbon-Air Battery Reaching an Output Power over 10 W and a Specific Energy of 3600 Wh kg^{-1}

Xiaomin Yan[a], Mingyang Zhou[a], Yapeng Zhang[a,b], Qianyuan Qiu[a,c], Qianyang Chen[a], Weizi Cai[d], Yubao Tang[e], Jiang Liu[a,*]

a. Guangzhou Key Laboratory for Surface Chemistry of Energy Materials, New Energy Research Institute, School of Environment and Energy, South China University of Technology, Guangzhou 510006, China

b. The Key Lab of Guangdong for Modern Surface Engineering Technology, National Engineering Laboratory for Modern Material Surface Engineering Technology, Guangdong Institute of New Materials, Guangzhou 510651, China

c. Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, Kemistintie 1, Espoo, P.O. Box 16100, FI-00076, Aalto, Finland

d. College of Engineering, South China Agricultural University, Guangzhou 510640, China

e. Key Laboratory of Optic-Electric Sensing and Analytical Chemistry for Life Science, MOE, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

*Corresponding author.

E-mail address: Jiangliu@scut.edu.cn

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Abstract

Carbon-air batteries have a very high theoretical specific energy. However, they have not been given sufficient attention because of the challenges associated with optimizing the battery design and making it rechargeable. Here we report a novel carbon-air battery stack based on solid oxide electrolyte which enables high operating temperature. The battery is composed of a tubular membrane electrode assembly (MEA), with a solid oxide electrolyte layer sandwiched between two porous electrodes, and carbon powder filled inside the MEA tube. By introducing a row of holes along the length direction of the MEA tube for current collection, the performance of the battery can be significantly enhanced because of shortened current paths. By using a removable quartz plug to stuff the open end of the MEA tube, the battery becomes mechanically rechargeable. Several batteries can be assembled into a stack by connecting the batteries in electrical series through the holes for current collection. A 3-battery-stack operating at 800 °C displays an output power of 11.0 W, corresponding to ~160 mW cm^{-2}. With an overall carbon powder of ~10 g, the stack discharges at 0.5 A and ~2.75 V for 26 h, revealing a specific energy of ~3600 Wh kg^{-1}, which is significantly higher than those of the state-of-the-art metal-air batteries.

Keywords: carbon-air battery, all-solid-state, tubular 3-battery-stack, improved current collection, mechanically rechargeable

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1. Introduction

In principle, the chemical energy of carbon can be efficiently converted into electrical power. The theoretical efficiency of this conversion, defined as the Gibbs energy change, ΔG, divided by the enthalpy change, ΔH, of the complete oxidation of carbon, is even slightly higher than 100%. It is significantly higher than that of a hydrogen-air fuel cell, especially at high operating temperatures, as shown in Fig. 1a.

It is also higher than the Carnot efficiency, even at high temperatures. Besides, the theoretical specific energy of carbon is high (~9293 Wh kg^{-1}). These superiorities of electrochemical oxidation of carbon inspire building up high performance carbon-air battery, for small scale applications such as portable power supplies and distributed power stations.

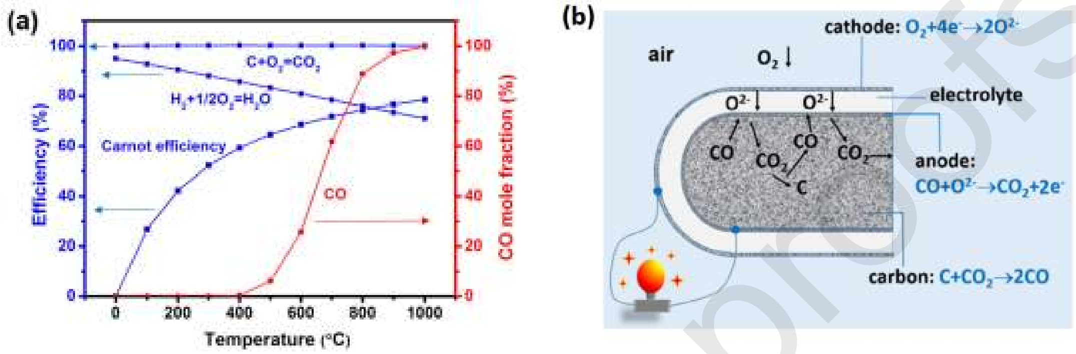

Fig. 1. (a) Theoretical conversion efficiencies of internal combustion engine (Carnot efficiency) and electrochemical oxidation of carbon and hydrogen (left axis, blue); Equilibrium gas composition of a C-O system with excess carbon (right axis, red). (b) A schematic illustration of the reaction mechanism of a carbon-air battery: Electrochemical oxidation of CO occurs at the anode to produce CO_2 and deliver electrons to the external circuit. The produced CO_2 diffuses to carbon to perform the reverse Boudouard reaction. Through the coupling of the two reactions, carbon is consumed and electricity is generated.

However, in practical, it is difficult to achieve the electrochemical oxidation of carbon because of the high activation energy (~190 kJ mol^{-1}) [1, 2]. High temperature is needed to accelerate the sluggish kinetics and therefore the electrochemical process is generally performed with molten salt [3-8], solid oxide [9-12], or hybrid [13-16] electrolytes. The technologies developed from these explorations are generally called direct carbon fuel cells (DCFCs) [17-20]. Most DCFCs involve either liquid medium,

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which may cause serious leakage and corrosion at high temperatures, or purging gas, which makes the system complex.

In recent years, the carbon-air battery with solid oxide electrolyte, also known as direct carbon solid oxide fuel cell (DC-SOFC) [9, 11, 21-23], has been attracting increasing attention because of its all-solid-state configuration and high performance. It simply consists of a membrane electrode assembly (MEA) of solid oxide fuel cell (SOFC), i.e., a solid oxide electrolyte layer sandwiched between a porous anode and a porous cathode, and solid carbon powder loaded in the anode chamber, as shown in Fig. 1b. Its feasibility is based on the fact that CO dominates the gas composition of a C-O system with excess carbon [24], as shown in Fig. 1a. The detailed equilibrium composition results from a thermodynamic calculation on the C-O system is shown in Fig.S1. Before operation, there is residual air in the intervals or pores of the carbon powder in the anode chamber. When a carbon-air battery is heated to 800 °C, the carbon will be oxidized to produce CO and CO_2, and the fraction of CO in the CO-CO_2 composition can reach 89% (Fig. 1a). Then, the CO will be electrochemically oxidized at the anode when the external electrical circuit is closed.

$$CO+O^{2-}=CO_2+2e^- \tag{1}$$

CO_2 produced from this electrochemical oxidation of CO diffuses to the carbon fuel to perform the reverse Boudouard reaction

$$CO_2+C=2CO \tag{2}$$

Combining eq. 1 and eq. 2, we obtain the overall anode reaction

$$C+2O^{2-}=CO_2+4e^- \tag{3}$$

This is a solid to gas reaction, suggesting that the pressure in the anode of an operating carbon-air battery is always higher than that of the surrounding air. In other words, the anode pressure is always positive.

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Several terminological names, direct carbon solid oxide fuel cell (DC-SOFC), carbon-air battery, and carbon-air fuel cell, may apply to the set shown in Fig. 1b [21]. It is called DC-SOFC because it is actually a solid oxide fuel cell (SOFC) directly operated with carbon as the fuel. There have been many efforts in developing DC-SOFCs for converting coal [25-28] and biomasses [29-33] into electrical power. However, it is still challenging to continuously provide solid fuels to DC-SOFCs [21, 33]. A DC-SOFC is also called as carbon-air battery, because if the carbon in the anode chamber and the MEA are integrated, it is actually a primary battery [23, 34-36]. From this point of view, it is similar to a metal-air battery [37-40]. Discharging capacity and specific energy are key characteristics for a battery. Similar to the situation that metal-air battery has been known as metal-air fuel cell, a carbon-air battery is also called as a carbon-air fuel cell [37]. In the present work, our focus is on the discharging performances and specific energy of the set. Therefore, we use the name “carbon-air battery”.

A carbon-air battery is similar to a metal-air battery that both of them have air cathode and solid-state anode active materials. However, they are different in several aspects: First, a carbon-air battery operates at high temperature while a metal-air battery generally works at room temperature. High operating temperature may accelerate the reaction kinetics to give high performance. It may also avoid use of expensive catalysts. Second, a carbon-air battery may use inorganic solid-state electrolyte while a metal-air battery usually uses liquid electrolyte. A solid electrolyte enables compact system and varieties in stack design. Third, the oxygen for oxidizing carbon will leave away from the carbon-air battery along with the produced CO_2, while the oxygen for oxidizing metal will stay in a metal-air battery, increasing the weight and reduce the energy density of the battery. Despite of the potential advantages of carbon-air batteries, there

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have been few efforts on their research and development mainly because of challenges in configuration design and rechargeable capability.

Here we report a novel compact mechanically rechargeable carbon-air battery reaching an output power of 11 W and a specific energy of 3600 Wh kg^{-1}. The designed carbon-air batteries are based on tubular solid oxide electrolyte, as schematically illustrated in Fig.2. It consists of a series of tubular MEAs in parallel. Each MEA tube is made of an electrolyte tube with one end closed and the other end open. An anode layer is applied inside the electrolyte and a cathode layer outside (Fig. 2a). The long tubular (i.e., the ratio of length to diameter is more than 5) MEA has the advantages of good mechanical strength, easy fabricating process, and high charge capacity of battery. However, the current collection of a long tubular MEA is a problem, especially for the anode. As shown in Fig. 2a, in a conventional tubular MEA, which is generally applied for an SOFC, current is collected through the collector (a material with superior electronic conductivity) located at the open end. The current paths, especially those from the points near the closed end, are long, causing a high electrical resistance. Generally, the sheet resistance of the cathode outside the electrolyte tube can be reduced by applying current collector, such as painting silver grids on the surface. However, it is difficult to apply current collector on the anode inside. To solve the problem, we propose a new way for collecting current, as shown in Fig. 2b and Fig. 2c. A series of holes are punched along the electrolyte tube during fabrication (Fig. 2b). These holes are used to fill current collector, for shortening the current paths. The improvement can be clearly seen by comparing the resistances of anode with the two collecting ways. The resistance of the anode with conventional current collection (Fig. 2a) is

$$R_{\mathrm{c}} = \rho \frac{L}{2 \times 0.5\pi D t} \tag{4}$$

where ρ is the resistivity of the anode, L is the length of the tube, D is the diameter and

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t is the thickness of the anode. Meanwhile, in the improved current collection (Fig. 2b), the current paths are along the semi-circle, and the resistance of the anode is

$$R_{\mathrm{i}} = \rho \frac{0.5\pi D}{2Lt} \tag{5}$$

The ratio of resistance of anode with conventional current collection to that with improved collection is

$$\frac{R_{\mathrm{c}}}{R_{\mathrm{i}}} = \left(\frac{L}{0.5\pi D}\right)^2 \tag{6}$$

For a tubular anode with a length of 10 cm and a diameter of 1.0 cm, as in the case of the present work, this ratio is over 40. Therefore, an improved performance can be expected from the battery with the novel current collection.

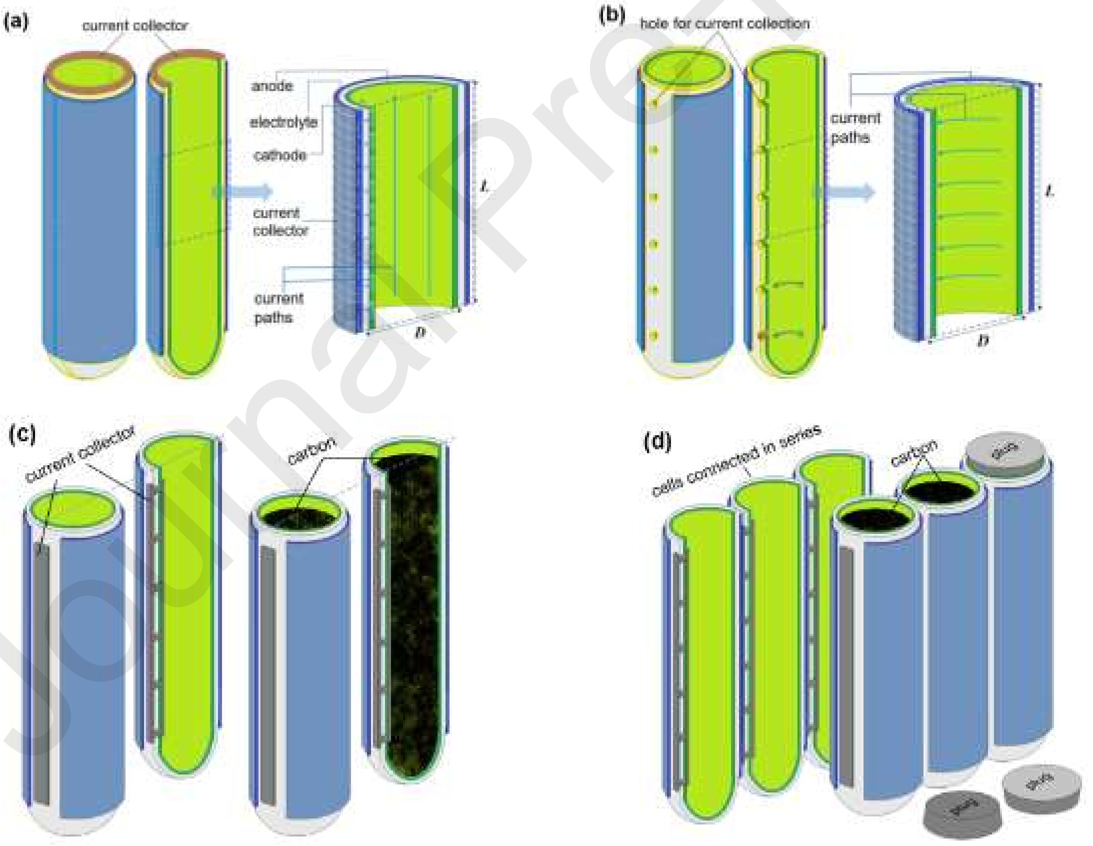

Fig. 2. Illustrations of tubular MEAs and carbon-air batteries: (a) A tubular solid oxide MEA with conventional current collection; (b) A tubular MEA with a series of holes along the electrolyte tube, for current collection; (c) A tubular carbon-air battery with

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improved current collection; (d) A stack of carbon-air battery, with three single batteries electrically connected in series, and removable quartz plugs.

A cylindrical carbon-air battery is built up by simply loading carbon inside a tubular MEA, as shown in Fig. 2c and Fig. 2d. Another important function of the holes for current collection is that it enables multiple MEAs to be electrically connected in series to form a stack, as shown in Fig. 2d. In the stack, the cathode of one MEA tube is connected to the anode of the next one, through the current collector material filled in the holes. Carbon powder is loaded inside the tubular MEAs and removable plugs, made of quartz, are used to cover the open ends. Note that, the electrolyte area near the electrical connecting holes is left blank, without cathode covering, to avoid short circuit between the anode and cathode. While this may lose some effective area of battery, the improved performance resulted from optimized current collection may compensate the loss. Despite this, the blank area should be kept as small as possible.

In the following, we report our work on fabricating the batteries and characterizing their output performances, discharging characteristics, thermal cycling durability, and rechargeable capability. Some corresponding key mechanisms are presented and analyzed in details.

2. Experimental

2.1 Fabrication of solid oxide MEAs

MEAs, with 1 wt.% Al_2O_3-doped YSZ electrolyte and Ag-GDC symmetrical electrodes, were prepared by dip-coating and brush-painting techniques [41]. A uniform electrolyte slurry was prepared by mixing Al_2O_3 and YSZ powder (in a weight ratio of 1:99) with ethanol (152 wt.% respecting to the powder), as solvent, polyvinyl butyral

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(PVB) (8%), as binder, triethanolamine (TEA) (3.2%), as dispersant, as well as dioctyl phthalate (DOP) (3.2%) and polyethylene glycol (PEG) (3.2%), as plasticizing agent, through ball milling for 3 h in a planetary ball mill (DM-4L, Nanjing Daran Technology Co. Ltd). A glass test tube was used as the mould. The test tube was vertically dipped down into the slurry. After 1 s, the tube, with a layer of slurry coated on its surface, was removed from the slurry. The layer of slurry on the tube was dried in the open air. This dipping-drying process was repeated eight times to form a green electrolyte with required thickness. Some of the as prepared green electrolyte tubes were directly removed from the mould. The others were punched to make a series of holes along the lengthwise direction of the tubes, before they were removed from the mould. The green electrolyte tubes were sintered at 1500 ºC for 4 h. The obtained YSZ electrolyte tubes were about 10 cm in length, 1.0 cm in diameter, and 150 μm in thickness. For the tubes with holes, the holes were ~1 mm in diameter and ~1 cm apart along the lengthwise direction. Meanwhile some short tubes, about 2.5 cm in length, without holes, were prepared.

A composite electrode paste of Ag-GDC was prepared by mixing silver paste (82 wt.% Ag), GDC (gadolinium doped ceria, $Ce_{0.9}Gd_{0.1}O_{1.95}$) powder, and PVB terpineol solution (concentration of 10 wt.%), in a weight ratio of 35:15:50, through grinding in an agate mortar for 4 h. Anode and cathode were respectively prepared on the inside and outside of the electrolyte tubes by brush-painting, using the Ag-GDC paste. The inside wall of each electrolyte tube was completely covered by the Ag-GDC electrode. To avoid short circuit, the edge part and the area near the holes were left blank when painting the outside of the tubes. The tubes with painted electrodes were calcined at 880 ºC for 2 h. Silver paste was applied to paint silver grids on the cathode as current collector. It was also used to draw a silver line, connecting, filling, and covering the

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holes of each tube to collect the current of anode. The effective area (or the area of cathode) of the long tubular MEAs without holes was 27 cm^2 while that of the MEAs with holes was 22.5 cm^2. The effective area of the short tubular MEAs was about 3.5 cm^2.

2.2 Preparation of carbon-air batteries and stacks

Activated carbon loaded with 5 wt.% of Fe, as catalyst [42], is used as the anode active material for carbon-air batteries and stacks. It was prepared by a wet agglomeration process [43]. Purchased activated carbon (Taishan Yueqiao Reagent Plastic Co. Ltd.) was pulverized in an electric grinder and sieved to obtain carbon powder of particles less than 200 μm. The activated carbon powder was mixed with Fe_2O_3 powder (A.R., Tianjin Kemiou Chemical Reagent Co., China) and PVB ethanol solution (concentration of 6 wt.%) by ball milling for 2 h, and then dried under an infrared lamp. The ratio of Fe to carbon is 5:95, and that of PVB to the Fe-C powder is 5:100.

The Fe-loaded carbon powder of 3.3 g was filled into each long tubular MEA to form a battery. A quartz plug, about 0.95 cm in diameter, was used to cover the open end of the batteries. To make battery stacks, silver paste was used as the interconnecting and jointing material [44] to connect the batteries in series. First, the holes along one MEA tube were covered by drawing a silver line along the direction of holes, as shown in Fig.2c. In this way, the holes were filled with silver that extends to connect the anode. Meanwhile, the holes were connected by the silver line. Then, the silver line was used to electrically and mechanically connect this MEA to the cathode of another MEA, as shown in Fig.2d. More MEA tubes were connected in the same way to obtain a stack. A 3-battery-stack is build up in this way, by filling 3.3 g of Fe-loaded carbon into each MEA tube and using quartz plugs to cover the open ends.

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The short tubular carbon-air batteries were attached to quartz tubes with diameter of 4 mm and 8 mm, respectively, to explore the outlet size influence on the performances of the batteries. 0.6 g of the Fe-loaded carbon was filled into each battery.

2.3 Characterization

The operating temperature for all the SOFCs and batteries is provided by an electric furnace (OTF-1200X, Kejing Materials Technology Co., Ltd, China). The long tubular MEAs, with and without punched holes, were firstly operated as SOFCs with humidified hydrogen (3 vol.% H_2O, 100 ml min^{-1}) as the fuel and ambient air as oxidant. Electrochemical performances of the SOFCs and the carbon-air batteries were characterized using Iviumstate electrochemical analyzer (Ivium Technologies B.V., Netherlands). The current-voltage characteristics were measured by cyclic voltammetry with a scan rate of 50 mV s^{-1} and a voltage range of 0.2-1.1 V (single battery) or 0.2-3.3 V (3-battery-stack). The electrochemical impedance spectra were measured by alternating current impedance technique in equilibrium with a frequency range of 0.1-10^5 Hz and a voltage amplitude of 10 mV. The duration characteristics were measured by constant current discharge method with a constant current of 0.5 A, 1 A, 2 A, and 2.5 A respectively. The microstructure of the tested cells was characterized using a scanning electron microscope (ZEISS SUPPRA 55VP, German).

3. Results and discussion

3.1 Performances of single batteries

Fig. 3a shows the as prepared YSZ electrolyte tubes, with and without current collecting holes, respectively. The MEAs (SOFCs) prepared using these tubes are shown in Fig. 3b. An SEM image of the section of an as prepared tubular MEA (Fig.S2) shows that the electrolyte is dense and its thickness is ~150 μm. Both the anode and

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cathode are porous and their thickness is about 50 µm. The tubular MEAs are firstly characterized as SOFCs using hydrogen as fuel and ambient air as oxidant. The output performances and the impedance spectra are shown in Fig.S3. An open circuit voltage of nearly 1.1 V and a reasonable output power (over 3 W) at 800 °C confirm the quality of the prepared MEAs.

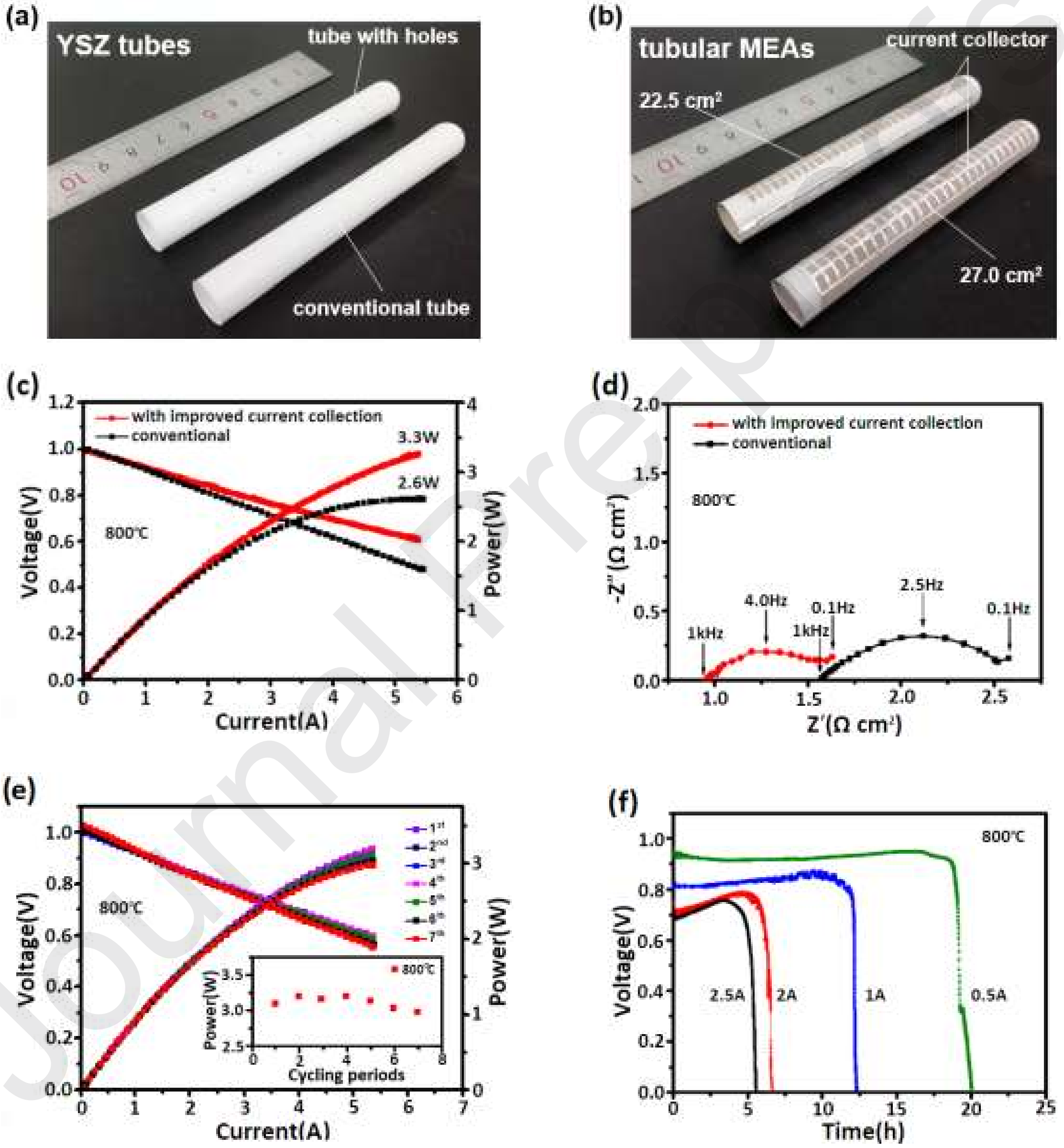

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Fig. 3. (a) YSZ electrolyte tubes with and without current collecting holes. (b) MEA tubes with novel and conventional current collection. (c) Performances of single tubular carbon-air batteries with improved and conventional current collection. (d) Impedance

spectra of carbon-air batteries with improved and conventional current collection. (e) Performances of a carbon-air battery with novel current collection during thermal cycling test. (f) Discharging characteristics of carbon-air batteries operating at a variety of electrical currents under 800 °C.

Fig.3c shows typical output performances of the carbon-air batteries, with the Fe-loaded activated carbon as the anode active material, at 800 °C. We tested several batteries and their performances, shown Fig.S4, have a good consistency. We can see from Fig.3c that, with an effective area of 27 cm^2, the battery of conventional current collection gives a peak power of 2.6 W (corresponding to a power density of 96 mW cm^{-2}) while that of the battery with improved current collection displays 3.3 W (147 mW cm^{-2}), although the latter battery has a smaller effective area, 22.5 cm^2. Obviously, the areal power density of a carbon-air battery is much enhanced by improving the current collection. This improvement is also verified by the impedance results shown in Fig. 3d. Compared to the areal specific resistance (ASR) of the battery with conventional current collection, 1.55 Ω cm^2, that of the battery with improved current collection is significantly reduced, which is only 0.95 Ω cm^2.

We test the thermal cycling performances of the tubular carbon-air battery with improved current collection. The battery is repeatedly heated from room temperature to 800 °C and then cooled down to room temperature for seven cycles. Fig. 3e shows the output performances of the battery at 800 °C for each cycle. The output power at 0.6 V maintains around 3.1 W, indicating that the carbon-air battery can be repeatedly started up and shut down. This is very important for portable application.

Fig. 3f shows the discharging characteristics of a carbon-air battery with improved current collection, operating at a variety of constant currents. Similar to that of a typical conventional battery (e.g., lithium ion battery), the discharging time and voltage flat

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increase with decreasing current. A carbon-air battery discharging at a constant current of 0.5 A gives a voltage flat of more than 0.9 V and a discharging time of about 20 h, leading to a capacity of 10 Ah and an energy of 9 Wh. As 3.3 g carbon is used in the battery, the obtained data mean that the utilization (or conversion efficiency) of carbon is 34% and the specific density of carbon is 2700 Wh kg^{-1}. Even the mass of the MEA, which is 4.7 g, is taken into account, the specific density is as high as 1125 Wh kg^{-1}, higher than that of the state-of-the-art Zn-air battery, 873.2 Wh kg^{-1}, a value obtained by only taking the mass of Zn into account [45].

Note that the voltage of the battery discharging at high current increases with discharging time. Two causes may be involved in the evidence: One is that the temperature of the battery increases because high operating current produces large amount of heat. The other is that high operating current results in high CO producing rate and the partial pressure of CO may increase in the anode chamber, leading to an increase of voltage.

The above battery performances are measured at relatively high temperature, 800 °C, because only at high temperature there is sufficient *in situ* produced CO for the anode reaction. In the anode chamber, CO dominates the composition when the temperature is higher than 700 °C. Meanwhile, both the partial pressure of CO and the ionic conductivity of the electrolyte of the battery increase with increasing temperature. Therefore, the carbon-air battery is discharged at 800 °C for gaining high performance. The performance of a carbon-air battery decreases significantly with reducing temperature. The output performances of a single battery operated at different temperatures are shown in Fig.S5. The measured peak power is 3.4, 1.4, and 0.4 W, at 800, 750, and 700 °C, respectively.

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3.3 Rechargeable capability

As mentioned above, the pressure in the anode chamber is always positive, which means that the carbon-air battery has no strict requirement on sealing. Actually, the open end of the tube is used as the outlet of the produced gas. However, there are two competing processes involving CO molecules in the anode of a carbon-air battery. One is that the CO molecules perform electrochemical oxidation at the anode. The other is that they may escape from the outlet. Which process dominates depends on the relative impedance of the two processes. When the outlet is of large size (wide), CO can easily escape through the outlet. Then more CO molecules will emit from the battery, without performing the electrochemical oxidation, causing voltage drop. On the contrary, if the outlet is narrow, more CO molecules will accumulate at the anode to perform the electrochemical oxidation. To confirm this speculation, we carry out an experiment comparing two carbon-air batteries, respectively with relatively wide and narrow outlets. The results (Fig. 4) show that the performance of the battery with narrow outlet is better, especially at high operating current. This suggests that reducing the size of outlet is important for obtaining high performance. We use a quartz plug stuffing the open end of a tubular battery. The outlet, which is the interval between the MEA tube and the plug, is much narrow. A comparison of the output performance of a battery, using plug to stuff the outlet, with a battery with a thin quartz tube of 4 mm in diameter as the outlet (Fig.S6) shows similar results.

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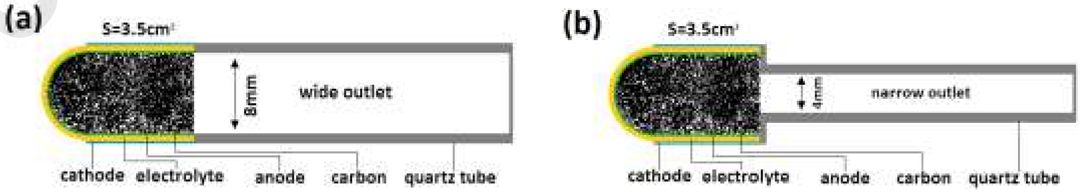

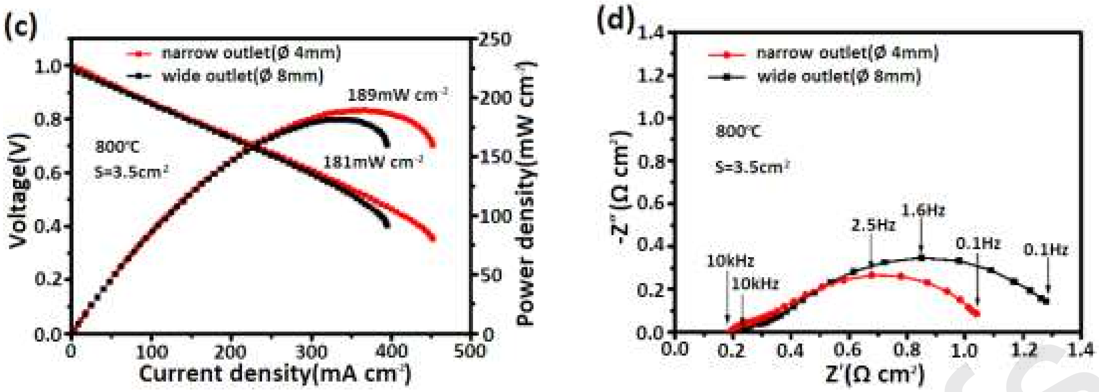

Fig. 4. Carbon-air batteries respectively with wide (a) and narrow (b) outlets. Output performances (c) and impedance spectra (d) of the carbon-air batteries operated at 800 °C. The short tubular batteries were about 2.5 cm in length, with an effective area of about 3.5 cm^2.

An important point of using a plug, rather than making a small hole as outlet, is that the plug is removable and carbon can be reloaded. Then the carbon-air battery becomes mechanically rechargeable. After the battery discharges completely under a constant current of 0.5 A, we remove its plug, decant the residue in the anode chamber, and reload a new batch of carbon powder. Then the battery discharges again at a constant current of 0.5 A. The characteristics of the battery for the first and second discharging processes are compared in Fig. 5. There is some degradation for the second discharging, with a lower average voltage flat of ~0.85 V. While the overall discharging time, 19.5 h, is close to that for the first discharging, the voltage flat is maintained for only 17 h. There might be two factors causing the degradation: One is the anode material, Ag-GDC. As the melting point of silver is only 961 °C and the operating temperature of the carbon-air battery is 800 °C, there might be some sintering of Ag, causing densification of the anode. The other is contamination of anode caused by impurities in carbon, such as alkaline metal oxides, through evaporation at the high operating

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temperature. Nevertheless, the initial work shows the carbon-air battery with a removable plug is mechanically rechargeable.

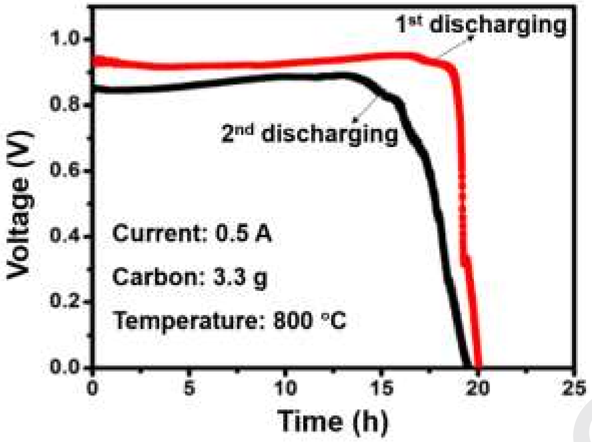

Fig. 5. Mechanical rechargeable performance of a single long tubular carbon-air battery discharging at a constant current of 0.5 A, under 800 °C.

3.4 Performances of 3-battery-stack

The working voltage of a single carbon-air battery is generally lower than 1.0 V. Therefore, connecting several batteries in electrical series is necessary to obtain required voltage for practical application. Shown in Fig.6a is a series of electrolyte tubes, with punches holes. Fig. 6b shows a stack with three MEA tubes connected in series. On this basis, we make a 3-battery-stack of carbon-air battery by filling 3.3 g of 5 wt.% Fe-loaded activated carbon into each MEA tube and stuffing the open end by using a quartz plug. Fig. 6c shows the output performance of the carbon-air battery stack operating at 800, 750. And 700 °C, respectively. At 800 °C, its open circuit voltage is over 3.0 V and its output power reaches 11.0 W under a voltage of 2.04 V. Taking the overall effective area of the 3-battery-stack as triple of 22.5 cm^2 (the effective area of a single battery), we calculate the areal power density of the stack and obtain 160 mW cm^{-2}. We also estimate the volumetric power density of the stack as 460 mW cm^{-3} through dividing the output power by the overall volume of the three tubular

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batteries, each with a diameter of 1.0 cm and a length of 10 cm. Similar to the situation of a single battery, the performance of the stack degraded significantly with reducing temperature. The output power of the stack at 750 °C is about 5.0 W and that at 700 °C is only 1.3 W.

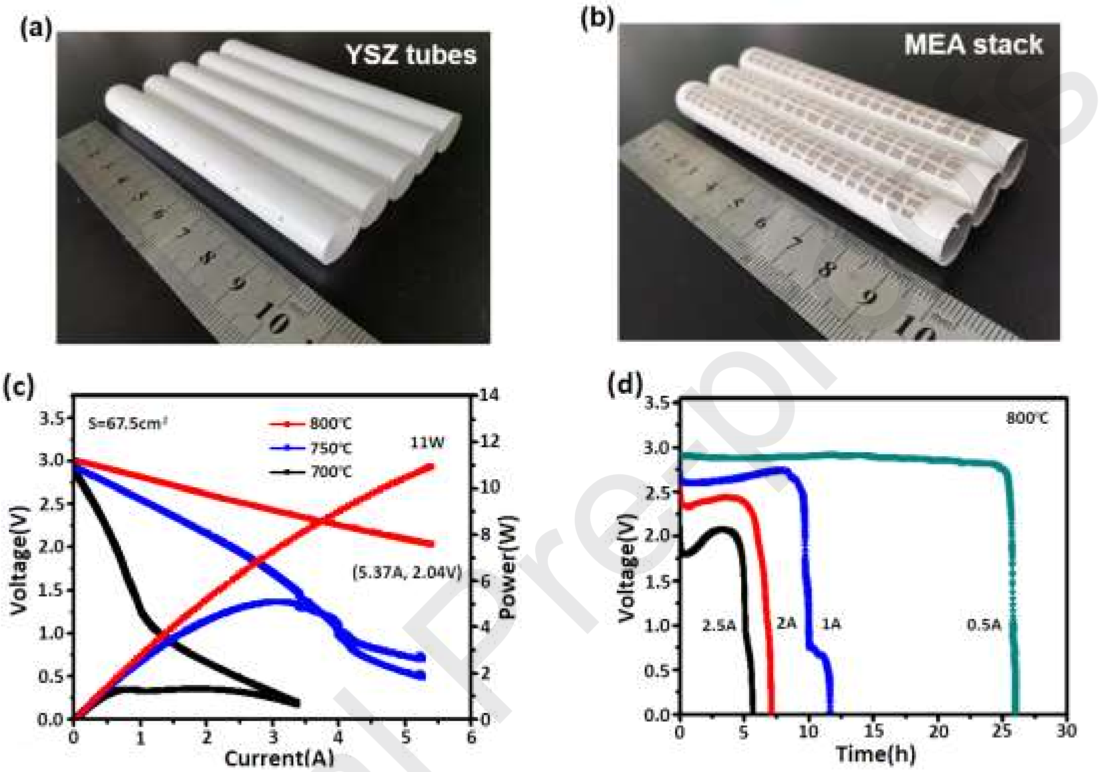

Fig. 6. (a) A series of YSZ tubes. (b) A stack of three tubular MEAs connected in series. (c) Output performances of a 3-battery-stack of carbon-air battery. (d) Discharging characteristics of 3-battery-stack of carbon-air battery discharging at a variety of electrical currents.

Fig. 6d shows the discharging characteristics of a carbon-air 3-battery-stack, operating at a variety of electrical currents, under 800 °C. The stack discharging at a constant current of 0.5 A gives an average voltage flat of 2.75 V. The discharging lasts for 26 h, resulting in a discharging capacity of 39 Ah. This corresponds to a carbon conversion efficiency (utilization of anode active material) of 44%, very high for such

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a small scale energy conversion devise. The electrical energy released from the battery discharging at 0.5 A is ~36 Wh, which means the specific energy of carbon of ~3600 Wh kg^{-1}. This practical specific energy of carbon-air battery is significantly higher than that of the state-of-the-art Zn-air battery (873.2 Wh kg^{-1}) [45] and the estimated practical specific energy of Li-air battery (600-900 Wh kg^{-1}) [38]. It is even larger than the theoretical specific energy of Zn-air battery (1353 Wh kg^{-1}) [39, 46]. The data for the battery stack discharging at a variety of currents are listed in Table 1. They show similar trend to conventional batteries, except that the discharging capacity and carbon conversion efficiency do not change much with operating current.

Table 1. Selected parameters for a 3-battery-stack of carbon-air battery discharging at a variety of electrical currents

Current (A)	0.5	1.0	2.0	2.5
Discharging voltage (V)	2.75	2.70	2.30	1.95
Discharging power (W)	1.88	2.70	4.60	4.88
Discharging time (h)	26	10	6.5	5.0
Discharging capacity (Ah)	39.0	30.0	39.0	37.5
Carbon utilization (%)	44	34	44	42
Discharging energy (Wh)	36	27	30	24
Specific energy (Wh kg^{-1})	3600	2700	3000	2400

4. Conclusions and prospects

Consequently, an initial investigation on the proposed carbon-air battery has shown its superior power density and specific energy in comparison to conventional batteries. There is still much room for further improvement of the battery performances: First, the thickness of the electrolyte can be reduced, e.g., from the present electrolyte-

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supported 150 μm to an anode-supported 10 μm, to decrease the ohmic resistance [47]. Second, the cathode can be optimized by applying catalysts to promote the oxygen reduction reaction (ORR), hence to reduce the polarization resistance of cathode. Third, the anode can be optimized by selecting proper catalysts for both the electrochemical oxidation of CO and the reverse Boudouard reaction. Although high temperature is needed to start up the carbon-air battery, the operating temperature may be self-maintained by the heat produced during discharging. More work is necessary in engineering management of heat and gas emission to make the carbon-air batteries acceptable for practical application, in portable power supplies or small power stations.

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Figure and Table Captions

Fig. 1. (a) Theoretical conversion efficiencies of internal combustion engine (Carnot efficiency) and electrochemical oxidation of carbon and hydrogen (left axis, blue); Equilibrium gas composition of a C-O system with excess carbon (right axis, red). (b) A schematic illustration of the reaction mechanism of a carbon-air battery: Electrochemical oxidation of CO occurs at the anode to produce CO_2 and electrons to the external circuit. The produced CO_2 diffuses to carbon to perform the reverse Boudouard reaction. Through the coupling of the two reactions, carbon is consumed and electricity is generated.

Fig. 2. Illustrations of tubular MEAs and carbon-air batteries: (a) A tubular solid oxide MEA with conventional current collection; (b) A tubular MEA with a series of holes along the electrolyte tube, for current collection; (c) A tubular carbon-air battery with improved current collection; (d) A stack of carbon-air battery, with three single batteries electrically connected in series, and removable quartz plugs.

Fig. 3. (a) YSZ electrolyte tubes with and without current collecting holes; (b) MEA tubes with novel and conventional current collection; (c) Performances of single tubular carbon-air batteries respectively with improved and conventional current collection; (d) Impedance spectra of carbon-air batteries with improved and conventional current collection. (e) Performances of a carbon-air battery with novel current collection during thermal cycling test; (f) Discharging characteristics of carbon-air batteries operating at a variety of electrical currents under 800 °C.

Fig. 4. Carbon-air batteries respectively with wide (a) and narrow (b) outlets. Output performances (c) and impedance spectra (d) of the carbon-air batteries operated

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at 800 °C. The short tubular batteries were about 2.5 cm in length, with an effective area of about 3.5 cm^2.

Fig. 5. Rechargeable performance of a single long tubular carbon-air battery discharging at a constant current of 0.5 A, under 800 °C.

Fig. 6. (a) A series of YSZ tubes. (b) A stack of three tubular MEAs connected in series. (c) Output performances of a 3-battery-stack of carbon-air battery. (d) Discharging characteristics of 3-battery-stack of carbon-air battery discharging at a variety of electrical currents.

Table 1. Selected parameters for a 3-battery-stack of carbon-air battery discharging at a variety of electrical currents

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Highlights

- A unique designed high performance and mechanically rechargeable carbon-air battery
- The battery based on long electrolyte tube has anode inside and cathode outside
- Current from anode is efficiently collected through holes along electrolyte tube
- Battery stack is formed by connecting single batteries in series
- A carbon-air 3-cell-stack gives output power 11 W and specific energy 3600 Wh kg^{-1}

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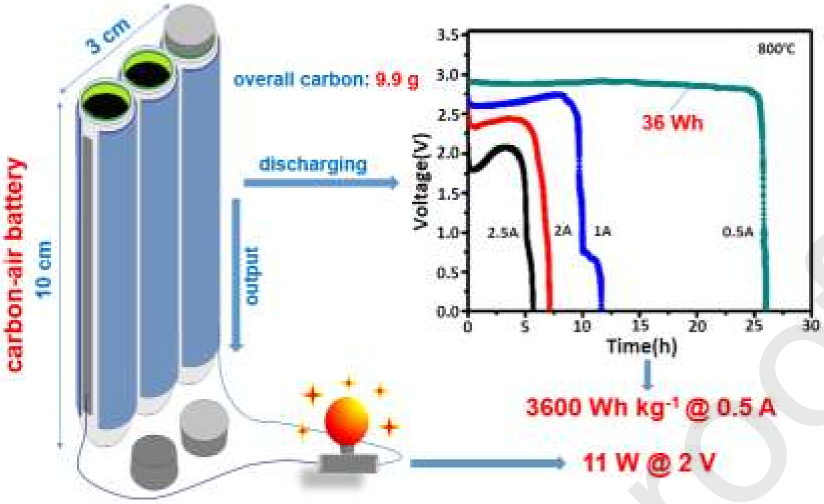
Graphical Abstract



A uniquely designed mechanically rechargeable all-solid-state carbon-air battery stack, with extremely high specific energy and power density, shows great promise for applications in portable power supplies and small power stations.

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