

Spray Coating Experiments: Setups and Methodologies







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Spray Coating Experiments: Setups and Methodologies, is the third in our Thin Films eBook series. This publication provides an introduction to spray coating, three article digests from Wiley Online Library and the latest news about Evident's Image of the Year Award 2022.

Wiley in collaboration with Evident, are committed to bridging the gap between fundamental research and industrial applications in the field of optical metrology. We strive to do this by collecting and organizing existing information, making it more accessible and useful for researchers and practitioners alike. Lithium-Air Batteries

A Lithium–Air Battery Stably Working at High Temperature with High Rate Performance

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Driven by the increasing requirements for energy supply in both modern life and the automobile industry, the lithium-air battery serves as a promising candidate due to its high energy density. However, organic solvents in electrolytes are likely to rapidly vaporize and form flammable gases under increasing temperatures. In this case, serious safety problems may occur and cause great harm to people. Therefore, a kind of lithium-air that can work stably under high temperature is desirable. Herein, through the use of an ionic liquid and aligned carbon nanotubes, and a fiber shaped design, a new type of lithium-air battery that can effectively work at high temperatures up to 140 °C is developed. Ionic liquids can offer wide electrochemical windows and low vapor pressures, as well as provide high thermal stability for lithium-air batteries. The aligned carbon nanotubes have good electric and heat conductivity. Meanwhile, the fiber format can offer both flexibility and weavability, and realize rapid heat conduction and uniform heat distribution of the battery. In addition, the high temperature has also largely improved the specific powers by increasing the ionic conductivity and catalytic activity of the cathode. Consequently, the lithium-air battery can work stably at 140 °C with a high specific current of 10 A g⁻¹ for 380 cycles, indicating high stability and good rate performance at high temperatures. This work may provide an effective paradigm for the development of high-performance energy storage devices.

The ever-growing demand on energy supply in both portable electronics and automobile industry is driving the revolution of high energy battery systems.^[1-4] Among various candidates, lithium–air battery has shown great potential due to its high specific energy.^[5,6] However, because of the open architecture of lithium–air batteries, organic solvents in electrolytes tend to rapidly vaporize and form flammable gases under the increasing temperature caused by the heat generated from the battery, which can bring in serious safety concerns.^[7–9] Active thermal management system such as forced cooling^[10] and self-protecting^[11] were reported to avoid the danger and keep the

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DOI: 10.1002/smll.201703454

batteries in desirable temperature ranges but would result in additional complexity. To this end, it is urgent while remains challenging to make lithium–air batteries that can tolerate high temperatures. Furthermore, the conventional lithium–air batteries are typically fabricated with a rigid bulk structure, which cannot meet the required flexibility and weavability in the next-generation flexible devices. In this case, a fiber format could be desirable for the lithium–air battery.

In this Communication, a novel fibershaped lithium–air battery with high thermal stability has been fabricated from ionic liquid gel electrolyte. Ionic liquids can offer wide electrochemical windows and low vapor pressures,^[12–16] as well as provide high thermal stability for the lithium–air batteries, enabling them to work at high temperatures. The gel made from polymer skeleton can enable uniform coverage which may help reduce leakage risk and improve interface contact.^[17,18] As a result, ionic liquid gel electrolyte would combine the advantage of ionic liquid and polymer gel, bringing both high thermal

and structural stability.^[19] In addition, the fiber format can offer both flexibility and weavability, and meanwhile realize rapid heat conduction and uniform heat distribution of the battery. Therefore, these batteries can work safely and stably at high temperatures, avoiding the complex system for heat dispersion. Besides, the high temperature has also largely improved their specific powers by increasing the ionic conductivity and catalytic activity of the cathode. Consequently, the lithium–air battery could work stably at 140 °C with a high specific current of 10 A g⁻¹ for 380 cycles, indicating high stability and good rate performance at high temperature.

The fiber-shaped lithium–air battery demonstrated a coaxial structure (**Figure 1**a). Lithium wire and aligned multiwalled carbon nanotube (CNT) sheet served as the anode and cathode, respectively, and a layer of ionic liquid gel electrolyte was sandwiched between them. The ionic liquid gel electrolyte was prepared by mixing ionic liquid of 1-*n*-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (BMPy-TFSI), lithium bis(trifluoromethylsulfonimide) (LiTFSI), and poly(vinylidene fluoride-*co*-hexa-fluoropropylene) (PVDF-HFP) with detailed preparation processes described in Experimental Section. The





Figure 1. The structure and working mechanism of the fiber-shaped lithium-air battery. a) The coaxial structure of the battery. b) Working mechanism of the battery during charging and discharging processes.

working mechanism of the fiber-shaped lithium–air battery is illustrated in Figure 1b. Briefly, during the discharging process, lithium metal on anode lost electrons and became Li⁺ which were then transported through the ionic liquid gel electrolyte and diffused toward cathode. At the cathode, assisted by the catalytic ability of CNTs, oxygen molecules extracted electrons from the external circuit to perform oxygen reduction reaction and combined with Li⁺ from electrolyte to generate LiO₂, which then disproportionated to Li₂O₂ (Figures S1–S3, Supporting Information). During the charging process, oxygen evolution reaction on cathode was driven by electrochemical potential via external circuit; Li₂O₂ lost electrons, releasing Li⁺ to the electrolyte and meanwhile oxygen to the air. The Li⁺ then transported through the electrolyte back to the lithium anode, where electrons were injected from external circuit and Li⁺ were reduced to Li.^[20]

Due to the high thermal conductivity of aligned CNTs and the unique one-dimensional (1D) configuration, the fiber-shaped lithium-air battery could be readily heated to a high temperature, e.g., 77 °C within 60 s (Figures S4 and S5, Supporting Information). The influence of temperature on rate performance of fiber-shaped lithium-air battery was carefully investigated firstly. The discharge voltage plateaus raised with increasing temperature from 25 to 100 °C (Figure 2a). When the specific current increased, the discharge voltage plateaus were well maintained at high temperatures in comparison to a rapid drop at low temperatures. At 100 °C, the discharge voltage plateaus were still quite flat even at a high specific current of 2 A g⁻¹, indicating good rate performances of the resulting device.^[21,22] Impressively. the initial discharge specific capacity reached 12 000 mA h g⁻¹, which was over four times higher than that derived from 25 °C (Figure 2b). These results show that high temperatures would enhance both rate and specific capacities of the resultant device. Apart from these, the lithium-air battery at high temperature also demonstrated good cyclic performance. For instance, the lithium-air battery could normally work at 100 °C for 100 discharge–charge cycles at 1 A g^{-1} (Figure 2c), compared with only 30 cycles at 25 °C under the same specific current (Figure 2d).

The good thermal stability of the ionic liquid enabled the gel polymer electrolyte to work stably at high temperature,^[23] and it worked properly in lithium–air batteries during multiple heating–cooling cycles, indicating their potential application in harsh environment (Figure 2e).

At high specific current, the inner resistance of the battery caused by charge and ion transfer becomes a major factor that limits the output power. For a better understanding on the batteries performance at high temperatures, electrochemical impedance spectroscopy (EIS) was performed to analyze the resistance in this system (**Figure 3**a). In EIS curves, the intercept point of the curve referred to electrolyte resistance, which was significantly reduced when the temperature increased (Table S1, Supporting Information). Arrhenius equation can be used to describe the correlation between temperature and conductivity of ionic liquid electrolytes^[24,25]

$$\log_{10}\sigma = \log_{10}\sigma_0 + 2.303 \frac{E_a}{RT}$$
(1)

where σ is the conductivity, σ_0 is a constant, E_a is the apparent activation energy, R is the universal gas constant, and T is the temperature in Kelvin. According to the calculations at Table S1 in the Supporting Information, the dependency of ionic conductivity on temperature fits Equation (1) well (Figure 3b). The ionic conductivity of the electrolyte was improved from 10^{-4} to 10^{-3} S cm⁻¹ when temperatures ranged from 25 to 100 °C. This increasing ionic conductivity was caused by the increasing ion mobility at higher temperature.^[14] Higher conductivity would bring lower inner resistance and therefore better rate performance,^[26,27] which agrees with our results.

To further investigate the reasons for high performances at high temperatures, cyclic voltammetry (CV) was performed from the aspect of electrochemical reaction potential. As shown in Figure 3c, a series of oxidation and reduction current peaks were observed. At certain scan rate, the diffusion coefficients would increase with the increase of temperature and eventually lead to higher specific current. The shift of the oxidative and reductive peaks at higher temperatures derives from the influences of thermodynamics and kinetics. Thermodynamically, according to Nernst equation, when the temperature increases, the reaction equilibrium potential would decrease.^[28] The gaps between oxidization and reduction peaks indicate that the battery system is controlled by both electron transfer and mass transfer.^[28] which lead to the decreased overpotential when the temperature increased.^[29] Under the combined effects, the CV curve would shift to lower potential when temperature increases, while the potential interval between oxidative and reductive peak would decrease at the same time. Therefore, the oxidative current peak in the CV curves moved toward the anodic reversing potential when temperature increased, while the reductive peak might move on either direction.

As a description of kinetically controlled reaction, Tafel equation can be used to describe the relation of overpotential and specific current when the overpotential η is larger than 118 mV and reaction happens under fast mass transfer^[28]

$$\eta = \frac{2.303RT}{\alpha nF} \log_{10} j_0 - \frac{2.303RT}{\alpha nF} \log_{10} j$$
(2)



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Figure 2. The electrochemical performance of the lithium–air battery at low specific current. a) Rate performance and b) initial discharge specific capacity at different temperatures. The cycle performances of the fiber-shaped lithium–air battery at c) 100 °C and d) 25 °C. e) Charge and discharge performances with the temperature switched between 25 and 100 °C repeatedly with a cutoff discharge specific capacity of 500 mA h g^{-1} for each cycle.

where *j* is the specific current, j_0 is a constant, α is anode or cathode transfer coefficient, *n* is the number of moles of electrons transferred in the reaction or half-reaction, *F* is the Faraday constant, η is overpotential, *R* is the universal gas constant, and *T* is the temperature in Kelvin. In the Tafel plot (Figure S6, Supporting Information), the curve at higher voltage shows that the specific current decreased linearly with increasing potentials. However, it reached a platform when the potential was lower than a threshold, indicating that mass transfer has become the rate-determining step. In Figure 3d, the relationship between potential and $\log_{10} j$ displayed a strong deviation from Tafel equation at room temperature, showing lower specific current than the log expectation and indicating that it had already reached the limitation of mass transfer at this specific current. However, this deviation was eliminated at high temperatures, and the maximal specific current had also been increased, indicating that high temperature promoted the electrochemical reactions and further enhanced the output performance of the battery.

Surprisingly, at a high temperature of 140 °C, the lithiumair battery shows satisfactory performances at the specific current of 10 A g⁻¹ (**Figure 4**a). Discharge–charge voltage plateaus of the battery show obvious difference when the temperature switched between 25 and 140 °C. At 25 °C, the discharge and recharge voltage plateaus were ≈1.8 and 4.9 V, respectively. After the temperature was increased to 140 °C, the discharge voltage plateau raised to ≈2.5 V and the recharge voltage plateau decreased to ≈4.0 V, demonstrating obvious decrease of the overpotential. When the battery was cooled down to 25 °C again, the performance deteriorated again as expected.





Figure 3. Electrochemical analysis of the lithium-air battery under increasing temperatures. a) Electrochemical impedance spectra of ionic liquid gel electrolyte at different temperatures. b) Dependence of the conductivity on temperature. c) Cyclic voltammograms and d) dependence of discharge plateau voltage on specific current at increasing temperatures from 25 to 100 °C.



Figure 4. The electrochemical performance of the lithium–air battery at a specific current as high as 10 A g⁻¹. a) Variation of the charging and discharging voltages with the temperature switched between 25 and 140 °C. b) Charging and discharging curves of a fiber-shaped lithium–air battery at 1st, 200th, and 380th cycles at 140 °C. c) Cyclic performance at 140 °C. A cutoff discharge specific capacity of 500 mA h g⁻¹ was applied in all the tests.

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However, once the temperature increased back to 140 °C, the performance recovered. This performance dependency on temperature kept good reversibility under many cycles of coolingheating processes. At the temperature of 140 °C, a remarkable cyclic performance of 380 discharge-charge cycles at the high specific current of 10 A g⁻¹ was shown at a cutoff specific capacity of 500 mA h g⁻¹. The discharge and charge curves at the 1st, 200th, and 380th cycles showed negligible capacity loss (Figure 4b,c), and the discharge plateau was mostly maintained within 380 discharge-charge cycles. In Figure 4c, the over potential at 140 °C increased from the 200th cycle to the 380th cycle, indicating an increase of the polarization upon cycling. The increased polarization, manifested by the increased difference between discharge and charge voltage plateaus, should be largely related to side reactions of the discharge product that would eventually lead to the performance failure.^[30]

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The fiber-shaped lithium–air batteries demonstrated better thermal stability beyond many other kinds of batteries. For lithium-ion batteries (LIBs), the highest working temperature has been increased to 90 °C by introducing additives to electrolyte,^[31] optimizing electrode material,^[32] using polymer electrolyte,^[33,34] or adding ionic liquids;^[35,36] for lithium–sulfur (Li–S) batteries, a general strategy was adopted by changing electrode materials,^[37,38] by which they could withstand a peak temperature of 70 °C. In the case of lithium–oxygen (Li–O₂) batteries, polymer electrolyte^[39] was employed to obtain a flexible battery and increased the working temperatures to 80 °C. Here, the working temperature has been largely extended to 140 °C, which is quite promising for applications in high-temperature environment. The details for batteries working at high temperatures are further summarized in Table S2 in the Supporting Information.

The specific energy and power of the fiber-shaped lithiumair batteries were also compared with their counterparts.^[40] The specific energy reached 3719 Wh kg_{cathode}⁻¹ with the weight of both carbon material and oxygen included in the calculation, which is nearly seven and two times higher than that of LIBs^[41–43] and Li–S batteries, respectively (Table S3, Supporting Information).^[44,45] In addition, they also demonstrated a high specific power of 7884 W kg_{cathode}⁻¹ with the weight of both carbon material and oxygen included in the calculation, which exceeded most of the other lithium–air batteries to the best of our knowledge (Table S4, Supporting Information).^[46–49]

In conclusion, through the employment of ionic liquid gel electrolyte and the design of a fiber format, a new type of lithium–air battery that can effectively work at high temperatures up to 140 °C has been developed. They demonstrated a good rate performance at a high specific current up to 10 A g⁻¹ and could work stably for 380 cycles at 140 °C with the high specific current of 10 A g⁻¹. This work also provided an effective paradigm for the development of other energy storage devices with high-temperature stability and rate performance.

Experimental Section

Preparation of Ionic Liquid Gel Electrolyte: Forty grams poly(vinylidene fluoride-co-hexa-fluoropropylene) (PVDF-HFP, $M_w = 400\,000$, Sigma Aldrich) was added into 60 g N-methyl-2-pyrrolidone (NMP) (AR, Sinopharm Chemical Reagent Co. Ltd.). The resulting mixture was then heated at 70 °C for 10 h to form a uniform solution (marked as Solution A).

2.87 g lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, 99 wt%, Aladdin) was dissolved in 3.19 g acetonitrile (AR, Sinopharm Chemical Reagent Co., Ltd.) and then mixed with 3.94 g 1-*n*-butyl-1-methylpyrro lidiniumbis(trifluoromethylsulfonyl)imide (BMPy-TFSI, >99%, Wuhu Nuowei Chemistry Co., Ltd.), followed by ultrasonic treatment for 5 min for preparation of a uniform solution (named as Solution B). Solutions A and B were then mixed with a weight ratio of 4/6 to produce the ionic liquid gel electrolyte.

Fabrication of Fiber-Shaped Li-Air Battery: A copper wire was partly inserted into a lithium wire (3.2 mm diameter, 99.8%, Alfa Aesar) serving as anode (Figure S7, Supporting Information). The lithium part was then dipped into the electrolyte and dried in an argon-filled glove box ($H_2O < 0.1$ ppm; $O_2 < 0.1$ ppm) at room temperature. The dipping and drying processes were repeated for three times, and the ionic liquid gel was dried under vacuum to form an efficient contact between the anode and electrolyte. During these processes, the weight of the fiber was monitored and the NMP was considered as eventually removed when the weight remains unchanged. The aligned CNT sheets were first drawn from a CNT array onto a polytetrafluoroethylene (PTFE) plate.^[50] The electrolyte-loaded lithium wire (Figure S8, Supporting Information) was then taken out of the glove box and rolled on this PTFE plate, and then wrapped with aligned CNT sheets (0.2 μ m) serving as the air cathode (Figure S9, Supporting Information) within 30 s. As shown in Figure S10 in the Supporting Information, the lithium foil coated with the ionic liquid gel electrolyte did not react with the ambient atmosphere for 30 min. Therefore, the electrolyte could function as a protective laver for the lithium metal from erosion during the 30 s of wrapping the aligned CNT sheet. The cathode was finally connected electrically through an aligned CNT fiber with the testing systems, and the preparation of CNT fiber was previously reported.[51]

Characterization: Scanning electron microscopy images were recorded from a Hitachi S-4800 operating at 1 kV. The electrochemical measurements were conducted on an Arbin multichannel electrochemical testing system (MSTAT-5 V/10 mA/16Ch). The CV measurements were carried out within a large electrochemical window of 1–5 V versus Li/Li⁺ at a scan rate of 2 mV s^{-1} . EIS was measured using a symmetrical stainless steel/electrolyte/stainless steel structure on an M204 Multi-Channel Autolab electrochemical workstation with applied voltage amplitude of 0.01 V and frequencies ranged from 0.1 Hz to 100 kHz. During all tests, the fiber-shaped lithium-air batteries were sealed in a box with molecular sieve and NaOH to get rid of water and CO₂. The relative humidity was 15%, where the discharge capacity was higher and the practical application could be more convenient than that in pure oxygen, although cycle performance was likely to be poorer.^[52] The specific capacity (C) was calculated by $C = (I \times t)/m_0$, where I, t, and m_0 represent the discharge current, discharge time, and weight of the CNT sheet electrode, respectively. The ionic conductivity (γ) of gel electrolyte was calculated from the equation of $\gamma = l/(R \times A)$, where I, R, and A correspond to the thickness, resistance, and area of gel electrolyte, respectively. The specific energy (E) of the lithium-air batteries was calculated from the equation of $E = (I \times t \times U)/m$, where *I*, *t*, *U*, and *m* represent the discharge current, discharge time, discharge voltage plateau, and weight of the CNT sheet electrode and reacted oxygen, respectively. The specific power (P) of the lithium-air batteries was calculated from the equation of P = E/t, where E and t represent the discharge specific energy and the discharge time, respectively.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

J.P. and H.L. contributed equally to this work. This work was supported by MOST (2016YFA0203302), NSFC (21634003, 51573027, 51403038,

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51673043, 21604012, 21503079), STCSM (16JC1400702, 17QA1400400, 15XD1500400, 15JC1490200) and SHMEC (2017-01-07-00-07-E00062).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

high rate performance, high temperature, lithium-air batteries, stable

Received: October 4, 2017 Published online: December 4, 2017

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