The cathode microstructure of Li-air battery plays a significant role in Li$_2$O$_2$ storage and electron transfer. In this article, we report a tunable three-dimensional hierarchically macroporous carbon nanotube foam as the air cathode. Excellent electrochemical performance with a specific capacity over 10,000 mAh g$^{-1}$ is achieved, which can be attributed to a combination of sufficiently large tunnels for oxygen transport and an appropriate pore width for oxygen reduction reaction. Also, an inverse correlation between the size of major pores and cell capacities is observed experimentally and a simplified analytical model is proposed to explain this correlation. Based on a combined study of galvanostatic discharge, microscopy, porosimetry, and modeling, we find that the discharge product Li$_2$O$_2$ is mainly deposited in the major pores of CNT foams.

The effects of the cathode microstructure on oxygen transport have been studied theoretically and experimentally by many research groups. Ye et al. found that Knudsen diffusivity can be influenced dramatically by pore size and suggested to use high porosity materials for improving oxygen diffusion.25,26 Li et al. also found that the effective diffusivity increases with porosity,27 Bardenhagen et al. observed restricted oxygen diffusion in mesopores and homogeneous discharge product deposition in macropores.28 Therefore, a porous carbon cathode with sufficiently large tunnels for oxygen diffusion, as well as an appropriate pore width for oxygen reduction is highly desirable. Recently, hierarchical air cathodes based on carbon nanotube (CNT)2,9 carbon black,13,14 honeycomb-like carbon,8,12 graphene oxide,10 and graphene15,16 have been reported with enhanced electrochemical performance.

In this work, a template-based method for manufacturing air cathodes with a wide distribution of pore size is reported. The cathodes are made of tunable CNT foams, in which the pores size distribution function can be easily controlled by the particle size of the microspheres template. In addition, the method can be used to fabricate cathodes with desired porosities. A series of cathodes with high porosity and different distributions of pore sizes were constructed and tested in Li-air cells for single galvanostatic discharge. The results of the electrochemical measurements were further combined with microscopy, porosimetry and modeling results to evaluate the role of pore size in Li$_2$O$_2$ deposition.

**Experimental**

**Material preparation.**—The CNT foams were fabricated based on the method reported earlier.31,32 Fig. 1 describes the synthesis pathway of the CNT foam. The multi-walled carbon nanotubes (MWCNT) were purchased from General Nano, LLC. The average length and the diameter of the MWCNTs are approximately 2 mm and 10 nm, respectively. The purity is higher than 99%. Polycrylonitrile (PAN), dimethylformamide (DMF), and isopropyl alcohol (IPA) were purchased from Sigma-Aldrich. PAN was dissolved in DMF to form a PAN/DMF solution with 1 weight percent of PAN concentration. The PAN/DMF solution was added to CNTs to achieve a weight ratio of PAN-to-CNT of 0.5 and then the appropriate amount of IPA was added.

**Electrochemical Society Member.**

**E-mail: zheng@eng.fsu.edu**

**Li-air batteries have attracted considerable attention in the past few years because of their high theoretical specific energies, which is approximately one order of magnitude higher than the specific energy of conventional Li-ion batteries.**1−3 The specific capacity of Li-air batteries can reach over 3,000 Wh kg$^{-1}$ that makes them attractive of many applications where oxygen is readily available, such as in portable electronic devices, transportation, and grid storage.4 Although Li-air batteries have a high theoretical specific energy they suffer from low power density, which, in practice, limits the range of their use. In order to increase the power density and cyclability of these batteries one needs to increase the oxygen transfer rate, improve the mechanical integrity of the cathode, and decrease the voltage losses across the solid Li$_2$O$_2$ layer formed during discharge. These improvements can be achieved in part by carefully designing the microstructure of the cathode to have high surface area and porosity and an optimum pore size distribution to increase oxygen diffusion.5−17 Although it is generally accepted that the pore size, surface area, and pore volume of the cathode material can affect the discharge capacity of Li-air batteries, their effects remain somewhat unclear. Some authors correlated the initial specific capacity with pore size, while other authors underlined the importance of surface area or pore volume.11,13,14,18−24 This apparent contradiction is due to the fact that the different research groups are using cathode materials with different pore size distributions, which results in different pore filling mechanisms during the discharge process. For instance, although micropores with a diameter smaller than 2 nm have extremely large surface area, their entrance is easily blocked by the reaction product Li$_2$O$_2$. Therefore, the flow of oxygen and Li$^+$ ions is often interrupted prematurely and these pores remain unfilled. For pore size in the order of 10 to 100 nm, there is a strong correlation between the specific capacity and the pore size as discussed in some research papers.18,23,24 Pores larger than a few hundred nanometers in size have a small surface area and are hardly being filled with reaction product. Therefore, these pores are essential for allowing the oxygen and Li$^+$ ions diffuse toward the reaction sites. For this reason, the performance of Li-air batteries cannot be determined by a single parameter but rather by the entire complex microstructure and pore size distribution of the cathode.
added to obtain the CNT/PAN/IPA mixture. The mixture was well dispersed by high power sonication (Misonix Sonicator 3000) for 30 min. Then, poly(methyl methacrylate) (PMMA) microspheres with the desired particle size and PMMA-to-CNT weight ratio were added to the CNT/PAN/IPA suspension and the mixture was subject to a 10-min bath sonication that helped it reach a uniform dispersion. After the sonication, the mixture was placed in a vacuum filtration system to make a CNT/PAN/PMMA solid composite, which was dried to remove the IPA and DMF completely. The CNT foams were obtained through a two-step heat treatment, first for 3 h in air at 300 °C and then for 1 h in nitrogen at 1200 °C with 80 ml min⁻¹ flow rate. During the first heat treatment, the PMMA microspheres were depolymerized and expelled while the PAN precursor was stabilized. In the second high-temperature treatment, the stabilized PAN precursor was carbonized to form a graphitic structure and accumulate at the joints of CNTs.

For comparison purposes, a similar procedure was applied to synthesize a CNT foam without regular spherical pores but of identical porosity, which is denoted as CNT-amorphous. Instead of using PMMA microspheres, the PMMA pallet (ACRYLITE 8N polymer) was dissolved and heated at 80 °C in acetone. Then, poly(methyl methacrylate) (PMMA) microspheres with the desired particle size and PMMA-to-CNT weight ratio were added to the CNT/PAN/IPA mixture. The mixture was well dispersed by high power sonication (Misonix Sonicator 3000) for 30 min. Then, poly(methyl methacrylate) (PMMA) microspheres with the desired particle size and PMMA-to-CNT weight ratio were added to the CNT/PAN/IPA suspension and the mixture was subject to a 10-min bath sonication that helped it reach a uniform dispersion. After the sonication, the mixture was placed in a vacuum filtration system to make a CNT/PAN/PMMA solid composite, which was dried to remove the IPA and DMF completely. The CNT foams were obtained through a two-step heat treatment, first for 3 h in air at 300 °C and then for 1 h in nitrogen at 1200 °C with 80 ml min⁻¹ flow rate. During the first heat treatment, the PMMA microspheres were depolymerized and expelled while the PAN precursor was stabilized. In the second high-temperature treatment, the stabilized PAN precursor was carbonized to form a graphitic structure and accumulate at the joints of CNTs.

Material characterization.—Scanning electron microscopy (SEM, JEOL-JSM7401F, 10 kV) was used to characterize the morphology of the CNT foams before and after discharge. The porosimetry of the CNT foams was measured using a surface analyzer (Autosorb IQ Micropore Instrument) with nitrogen gas adsorption-desorption at 77K. All samples were outgassed at 200 °C for 2 h prior to the measurement. The Brunauer–Emmett–Teller (BET) surface areas were determined from the linear portion of the adsorption isotherm. The pore size distributions were calculated using the Barrett–Joyner–Halenda (BJH) method applied to the adsorption branch of the isotherm. The total pore volumes were measured at relative pressure p/p₀ = 0.995. The phase identification of the discharge product was conducted by the wide angle X-ray scattering (WAXS) experiments, which were performed on a Bruker NanoSTAR system with an Incoatec 1-Pro microfocus X-ray source operating at 45 kV and 650 μA. The primary beam was collimated with cross-coupled Göbel mirrors and a 3-pinhole collimation system, providing a Cu Kα radiation beam (λ. = 0.154 nm) with the beam size about 0.15 mm at the sample position. The wide angle pattern and intensity were captured by a photo image plate, and read with a FLA-7000 scanner. Previous to the analysis, the discharged cathode was washed with TEGDME solvent and dried in the glove box. The sample was transferred into the WAXS chamber and evacuated within 30 secs to reduce the reaction of the Li₂O₂ with moisture and CO₂ in the ambient atmosphere.

Electrochemical characterization.—The CNT foams were directly punched to disks with a diameter of 0.625 inch (15.875 mm) and used as cathodes for the Li-air batteries studies in this work. A Li-air cell was built in an argon atmosphere glove box (MBraun) by stacking a lithium metal anode (Alfa Aesar, 99.9%, 0.75 mm thickness), a piece of glass fiber separator (EL-CELL GmbH, Co, Germany, 1.55 mm thickness), and a punched CNT foam cathode disk into an electrochemical testing cell (ECC-AIR, EL-CELL GmbH, Co, Germany). A stainless-steel ring spacer was used to set the thickness of the cathode to 100 μm. The organic electrolyte was made using 1 M LiCF₃SO₃ (Sigma Aldrich, 99.995%) in TEGDME (Sigma Aldrich, 99%).

The discharge measurements were carried out in 1 atm. oxygen gas at room temperature using an Arbin Instrument (Arbin-010 MTS pro 4.0-BT2000) controlled by a computer. The fresh Li-air cell was discharged to 2 V at a selected discharge current density. The specific capacities were calculated based on the weight of cathode materials without electrolyte.

Results and Discussion

Multiple CNT foams with different distribution of pore sizes were fabricated by adjusting the particle size of PMMA microspheres and keeping the weight ratio of PMMA-to-CNT constant. In this work, the diameters of PMMA microspheres were 6 ± 2, 9 ± 2, 19 ± 2, 23 ± 2, and 27 ± 2 μm. The samples obtained in this way were denoted as CNT6, CNT9, CNT19, CNT23, CNT27, respectively. The CNT foam prepared with PMMA pallet was denoted as CNT-amorphous. The sample porosity was ca. 98% and the thickness before assembly was ca. 200 μm.

The cross-sectional SEM images of the various pristine CNT foams are presented in Figs. 2a–2e. The cellular microstructure of CNT foams consists of relatively large spherical voids (called major pores, in micro-meter size), which are formed at the initial sites of the PMMA templates. During the thermal treatment, the PMMA microspheres are removed from the composite at temperature below 300 °C and the thermal degradation of PMMA microspheres does not have an significant impact on the surface composition of CNTs (see the Supplementary Material). The major pores are close-packed and interconnected with each other through junctions of carbonaceous walls. One can see that the dimensions of spherical voids depend on the PMMA templates size and that the morphology of CNT foams can be easily modulated by adjusting the diameter of PMMA spheres, while keeping the weight ratio of PMMA-to-CNT constant. The frequency and periodicity of the major pores depends on the concentration and arrangement of the PMMA microspheres. It is worth noting that because the length of CNTs is much longer than the diameter of the PMMA microspheres and the CNTs and PMMA microspheres are deposited layer by layer during the vacuum filtration process, the major pores do not match exactly the shape of the PMMA microspheres. The above observations under SEM imaging indicate that the morphology of pristine CNT foams agrees well with the structure proposed in the schematic in Fig. 1. Higher resolution scans of the CNT foams indicates that the prepared CNT foams with different PMMA microspheres exhibit similar nano-scale structure and in Figs. 2f–2h we present the SEM
Figure 2. SEM images of the CNT foam cathode. (a-e) Cross-sectional image of sample CNT6; CNT9, CNT19, CNT23, and CNT27; and (f-h) SEM images of sample CNT6 with higher magnifications.

Table I. Surface area and pore characteristics of CNT foam samples.

| cathode material | surface area (m² g⁻¹) | pore volume (cm³ g⁻¹) | average pore size (nm) | specific capacity (mAh g⁻¹) |
|------------------|------------------------|-----------------------|------------------------|-----------------------------|
| CNT6             | 425                    | 2.45                  | 38.8                   | 10390                       |
| CNT9             | 358                    | 1.79                  | 30.8                   | 8291                        |
| CNT19            | 445                    | 2.66                  | 32.9                   | 6217                        |
| CNT23            | 431                    | 2.29                  | 32.4                   | 4635                        |
| CNT27            | 451                    | 2.06                  | 24.7                   | 3330                        |

images of CNT6 samples with higher magnifications. Fig. 2g displays a typical major pore in the CNT6 sample, which clearly shows that the walls of major pores are made of CNTs and contain numerous nano-scale pores. The randomly entangled CNT structure (see Fig. 2h) greatly improves the surface area of the material.

The porosimetry of the CNT6-27 cathodes was then studied using the nitrogen adsorption-desorption method. Fig. 3a presents the isotherm curves for sample CNT6, but the curves for all the other CNT foam samples are very similar. These isotherm curves are of type IV according to International Union of Pure and Applied Chemistry (IUPAC) classification of six sorption isotherms. They suggest that the CNT foam contains primarily meso- and macropores, consistent with the structure observed by SEM. The BJH pore size distributions of CNT foam samples are shown in Fig. 3b. Obviously, the pore size distributions of all the materials share a similar shape despite their distinct morphologies in micro-scale range. In addition, the volume fraction of the micropores is very small and the macropores occupy a significant fraction of pore volume, which should improve oxygen transport in these materials. Table I summarizes the measured results of surface area, pore volume, and average pore size. CNT27 exhibits the highest value of the BET surface area, which is 451 m² g⁻¹. CNT19 has the highest pore volume of 2.66 cm³ g⁻¹. On the other hand, CNT9 shows the lowest value for the surface area and pore volume. Note that the present method can only measure pore widths up to 300 nm, and therefore can only characterize micropores (<2 nm), mesopores and macropores.

Figure 3. Porosimetry result by nitrogen adsorption and desorption method. (a) Isotherm of sample CNT6; (b) BJH pore size distributions of CNT foam samples; and (c) An illustration of pore width in CNT foam and in measurement.

Downloaded on 2019-04-27 to 207.241.231.82 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).
As described in the previous section, the freestanding CNT foams were directly punched to disks and used as air cathodes for galvanostatic discharge. Li$_2$O$_2$ was determined as the main products after discharge with no other significant byproducts, e.g., LiOH and Li$_2$CO$_3$, detected as evidenced by the WAXS profile of discharged CNT6 cathode in Fig. 4. Although not included here, the other CNT cathodes display similar WAXS patterns. The peaks at ca. 22° and ca. 38° are from the carbon peaks with index of (002) and (100), respectively. Fig. 5 presents the discharge voltage profiles of the Li-air cells assembled from the carbon peaks with index of (002) and (100), respectively. Fig. 4 presents the discharge voltage profiles of the Li-air cells assembled from the carbon peaks with index of (002) and (100), respectively. Although not included here, the other CNT cathodes display similar WAXS patterns. The peaks at ca. 22° and ca. 38° are from the carbon peaks with index of (002) and (100), respectively. Since the discharge profiles show a clear inverse correlation between the major pore size and the specific capacity, while all the other parameters characterizing the microstructure of the cathodes have relatively similar values (see Table I), it can be concluded that the major pores are responsible for the capacity difference between the different cathodes.

The CNT foam has many characteristics that account for its outstanding capacity performance. First, the excellent electron transport properties of individual CNTs and the effective crosslinks between CNTs result in the high electrical conductivity of the material. The high surface area given by the high density of nano-scale pores forming the wall of the major pores favors the discharge reaction. The large void volume provides sufficient storage space for Li$_2$O$_2$. The freestanding architecture eliminates the problems related to binder decomposition during cell operation. The three-dimensional macroporous CNT network promotes the efficient electrolyte wetting.

Another critical function of major pores in the CNT foam is to promote oxygen transport. The non-uniform deposition of the discharge product is regarded as one of the main drawbacks of Li-air batteries and is directly related to the diffusion length of the oxygen in the electrolyte. Since oxygen diffusion length increases with the proportion of major pores, the major pores ensure a continuous, pore clogging free oxygen flow to the inner regions of the cathode and act as a “highway” for oxygen supply. For this reason, in structures with a high proportion of major pores, the discharge product is likely to deposit near these large pores and the deposition throughout the cathode is more uniform. To study the property of CNT foams after discharge, we select the CNT6 cathode and CNT27 cathode, which has the highest and lowest discharge capacity in the set of prepared CNT foams, respectively. Despite a difference in the volume density of solid product, the overall morphology of the discharged air cathodes is quite similar and Fig. 6 shows the SEM images of CNT6 cathode surface (the corresponding SEM images for CNT 27 samples are shown in Fig. S3 in the Supplementary Material). As seen in Fig. 6a, the carbon surface was deposited with discharge product while major pores remain open, suggesting pore volume was not fully exploited. The surface coverage condition was compared at the separator side and the air side was illustrated in Figs. 6b–6d. The surface at the air side was covered almost completely by Li$_2$O$_2$ and the corresponding porosity in this region dropped to nearly zero. The surface at the separator side was also covered with a significant amount of Li$_2$O$_2$, although a small number of open pores were still visible. The higher magnification image in Fig. 6d shows the morphology of densely-packed Li$_2$O$_2$ particles, which has sub-micro particle sizes. The SEM image of CNT6 cathode at a depth of discharge of 25% (see Fig. S4 in the Supplementary Material) indicates small Li$_2$O$_2$ particles were

Figure 4. WAXS profile of discharged CNT6 cathode.

Figure 5. The first discharge voltage profiles of Li-air batteries with CNT foam cathodes at a current density of 0.13 mA cm$^{-2}$.

Figure 6. SEM images of discharged CNT6. (a) Cross-sectional image of discharged CNT6; (b) Image of discharged CNT6 surface at the separator side; (c) Image of discharged CNT6 surface at the air side; and (d) Higher magnification image of discharged CNT6 surface at the air side.
formed, and eventually coalesced and fully covered the electrochemical reaction sites, in agreement with other reported papers.36–38 These images demonstrate that the oxygen diffusion rates are significantly increased in the presence of major pores and the size of major pores does not affect the distribution of the discharge product significantly.

The function of the major pores is further demonstrated by comparing the electrochemical performance of a CNT6 cathode with a CNT-amorphous cathode at different discharge currents. The CNT-amorphous cathode was synthesized with a similar procedure expect that the PMMA microspheres were replaced with PMMA pellets. As seen in the SEM images in Fig. S5 in the Supplementary Material, the PMMA template has an amorphous morphology without any periodical macroscopic shape, the obtained cathode does not possess any regular spherical voids. Therefore, the CNT-amorphous cathode has an identical porosity with above-mentioned CNT foams while the major pores no longer exist. It is also obvious that in the absence of PMMA microspheres, the CNTs are distributed much less uniformly throughout the foam. As seen in Fig. 7, in the presence of major pores, the CNT6 cathode delivered significantly higher capacities at all the current densities. In fact, CNT-amorphous cathode delivers a specific capacity even lower than the CNT27 cathode, which suggests that the role of the major pores is essential to promote oxygen transport and increase the discharge capacity. The enhanced rate capability of CNT6 sample under all the discharge currents indicates that the optimized major pores will alleviate the issue of oxygen transport limitation at high discharge currents.

It is also of interest to analyze the dependence of specific capacity on the microscopic parameters of the CNT foam, in particular, on the size of the nano-scale pores, surface area, total pore volume, and the radius of the major pores. Correlation analysis was conducted between specific capacities of the cells and the other parameters showed in Table I. The results of this analysis show that specific capacity is strongly correlated with the radius of the major pores (the magnitude of the Pearson coefficient is above 0.98, see the Supplementary Material) and weakly correlated or uncorrelated with the remaining variables. This observation suggests again that the major pores play the most important role in the final value of the capacity and that the discharge product deposits mostly inside these pores.

The fact that capacity decreases monotonically with the radius of the major pores can be explained using the following simplified model. Let us assume the cathode is made of major pores with radius $R$, which are uniformly distributed throughout the material. After assembly, the major pore will be compressed and will become an oblate spheroid with radius $a = b = R$ and $c = \alpha R$ ($\alpha < 1$). The discharge product is assumed to deposit uniformly on the inner surface of these pores by forming a solid layer of thickness $t$ and area $S$. Using the approximate formula of oblate spheroid surface area (see the Supplementary Material), $S$ is equal to $S = \frac{3\sqrt{3}a \pi c^2}{4}$. Therefore, the total volume of the major pores is $V_k = \frac{3\pi}{2}a^2 c$, where $a = R$. During the discharge process the thickness of the deposit layer increases continuously, which results in an increase of the voltage drop across the deposit layer. As predicted by a number of density function theory (DFT) calculations and numerical simulations the battery “dies” when the thickness of the deposit layer reaches a critical value, $t_{\text{max}}$. The volume of the Li2O2 deposited in the major pores when the battery “dies” is equal to $V_{\text{Li2O2, major}} = t_{\text{max}} V_k$.

During the discharge both the nano-scale and major pores are filling in with Li2O2. Due to the similarity of the nano-scale pore structure, the volume of the Li2O2 deposited in the nano-scale pores is assumed constant. Therefore, the total volume of Li2O2 is equal to

$$V_{\text{Li2O2}} = V_{\text{Li2O2, nano}} + V_{\text{Li2O2, major}} = V_{\text{Li2O2, nano}} + \frac{3(1+c^2)}{2} t_{\text{max}} V_k \frac{1}{\alpha}$$

At the same time, $V_{\text{Li2O2}}$ can be expresses as $V_{\text{Li2O2}} = \frac{1.66 m_F \rho F}{2 \rho d}$, where $Q$ is the specific capacity (in mAh g$^{-1}$), $m_F$ is the weight of the cathode, $M_F$ is the molar weight of Li2O2, $\rho$ is the bulk density of Li2O2. $F$ is the Faraday constant. It follows that the discharge capacity $Q_d$ (in mAh) can be expressed as

$$Q_d = Q m_F = \frac{2V_{\text{Li2O2}} \rho F}{3.6 M_d}$$

$$= \frac{2 \rho d F}{3.6 M_d} \left( V_{\text{Li2O2, nano}} + \frac{3(1+c^2)}{2} t_{\text{max}} V_k \frac{1}{\alpha} \right) = a + \frac{b}{R^\alpha}$$

where $a$ and $b$ are parameters that depend on the geometry and material properties of the cell.

The contribution of the nano-scale and major pores to Li2O2 deposition appears explicitly in the last two terms of Eq. 2. This equation also shows that the capacity of the cell is inversely proportional to the radius of the major pores when $\alpha$ is a constant. Parameters $a$ and $b$ can be determined by fitting the experimental data with Eq. 2.

The CNT foams possess outstanding mechanical properties due to the crosslinking effect and ordered porous structure in CNT foam.31,32 As a result, a compression rate of up to 90% of its initial thickness (i.e., $\alpha = 0.1$) can be achieved. Fig. 8 presents the discharge capacity of the cells with CN6-CNT27 cathodes as a function of the characteristic pore length $L$. The characteristic pore length $L$ is defined as $L = \sqrt{S V_t}$. For these cells, $\alpha \approx 0.5$ since the thickness of the cathode was compressed from ca. 200 μm to 100 μm. The experimental values of the capacity were calculated from Table I and are denoted with symbols in Fig. 8a, while the fitted values given to Eq. 2 are plotted using a continuous line. The fitting was done using the nonlinear least squares method for which an R-squared value of 0.977 was obtained. Among the five samples, CNT6 has the largest capacity contribution from major pores because of its high major pores surface area. CNT27 has the smallest contribution from major pores, with only ca. 40% of discharge capacity being due to major deposition. Therefore, a method to increase the specific capacity of Li-air batteries is to use cathodes with major pores for enhanced oxygen transport and Li2O2 deposition. Although for major pores larger than a few micrometers, the discharge capacity increases when the size of the pores decreases, it is expected that the discharge capacity will deteriorate if the size of these pores decreases below a few hundred nanometers to one micrometer. This phenomenon is due to the fact that the tortuosity of the material increases in the absence of large pores, while the effective value of oxygen diffusion coefficient decreases. In order to verify the assumption, two additional CNT6 cathodes with increased initial thickness

![Figure 7](https://example.com/figure7.png)  
**Figure 7.** The first discharge capacity of Li-air batteries with CNT6 cathode and CNT-amorphous cathode at different current densities.
Figure 8. Fitting result of $Q_1$ with respect to characteristic pore length.

(c.a. 400 μm and 600 μm, and denoted as CNT6-2\* and CNT6-3\*, respectively) were synthesized by keeping the weight of CNT constant and increasing the weight ratio of PMMA-to-CNT. During the cell assembly, the cathodes were compressed to the same thickness of 100 μm to ensure they have identical porosity with CNT6-CNT27 cathodes but have reduced characteristic pore length due to a smaller value of $\alpha$. The capacities of CNT6-2\* and CNT6-3\* do not show significant change despite the reduced characteristic pore length (see Fig. S6 in the Supplementary Material). Next the experimental results are compared with the modeling values in Fig. 8b. It is obvious that the specific capacity only slightly increases and then decreases when $L$ is further reduced, which clearly departs from the modeling prediction as seen in the dashed line region in Fig. 8b. It is likely that for CNT6-2\* and CNT6-3\* cathode, the oxygen diffusion coefficient is already considerably reduced and therefore our simplified mathematical model is accurate only for sufficiently large characteristic pore lengths (i.e., in the solid line region in Fig. 8b).

Despite having a large specific capacity of over 10,000 mAh g$^{-1}$, the CNT foam is less attractive when considering the volumetric capacity, since the electrolyte will flood the void of the cathode and consequently the electrolyte weight will dominate the total cell weight. In addition, a significant amount of electrolyte will be displaced to accommodate the solid product after the discharge process, which is a challenging issue for practical cells of this system. The practical void volume (i.e. the porosity) needs to be optimally designed for practical applications. Using a partially wetted electrode can potentially address this issue caused by the flooded electrolyte.\textsuperscript{35} Moreover, to further enhance the rate and cycle performance of the Li-air cells, it is suggested to use an efficient catalyst loaded in the optimized CNT foam cathode.\textsuperscript{42,43}

Conclusions

A macroporous CNT foam obtained using a template-based method is reported and used as the air cathode in Li-air batteries. It is shown that the reported CNT foam can deliver a specific capacity over 10,000 mAh g$^{-1}$, which is among the highest values reported in the literature. This high specific capacity is due to the hierarchical structure of the CNT foam, which contains both nano-scale and major pores in micro-meter size. The major pores are essential in enhancing oxygen diffusion and maximizing pore utilization. In addition, an inverse correlation between the size of the major pores and the cell capacities is observed experimentally and modeled analytically. SEM and porosimetry measurements are conducted and combined with the modeling results to analyze the Li$_2$O$_2$ deposition process inside the cathode. The results highlight the significance of building a hierarchical pore structure for the air cathode, with large pores for oxygen transport and small pores for Li$_2$O$_2$ deposition. It is believed that further enhanced electrochemical performance can be achieved by optimally designing the structure of the major pores and loading the cathode with an effective catalyst.

Acknowledgments

This work was supported by US Army Power Division [grant numbers GTS-S-15-014] and the National Science Foundation [grant numbers 1609860].

ORCID

Jim P. Zheng \(\text{https://orcid.org/0000-0003-2689-0067}\)

References

1. J. Christensen, P. Albertus, R. S. Sanchez-Carrera, T. Lohmann, B. Koziyons, R. Liedtke, J. Ahmed, and A. Kojic, J. Electrochem. Soc., 159, R1 (2012).
2. L. Grande, E. Paulard, J. Hassoun, J. B. Park, Y. J. Lee, Y. K. Sun, S. Passerini, and B. Scrosati, Adv. Mater., 27, 784 (2015).
3. K.-N. Jung, J. Kim, Y. Yamauchi, M.-S. Park, J.-W. Lee, and J. H. Kim, J. Mater. Chem. A, 4, 14050 (2016).
4. J. P. Zheng, R. Y. Liang, M. Hendrickson, and E. J. Pichta, J. Electrochem. Soc., 155, A432 (2008).
5. W. Zhou, H. Zhang, H. Nie, Y. Ma, Y. Zhang, and H. Zhang, ACS Appl. Mater. Interfaces, 7, 3389 (2015).
6. B. Sun, S. Chen, H. Liu, and G. Wang, Adv. Funct. Mater., 25, 4436 (2015).
7. Z.-L. Wang, D. Xu, J.-J. Xu, L.-L. Zhang, and X.-B. Zhang, Adv. Funct. Mater., 22, 3699 (2012).
8. Y. Li, X. Li, D. Geng, Y. Tang, R. Li, J.-P. Dodelet, M. Lef`evre, and X. Sun, Carbon N. Y., 64, 170 (2013).
9. X. Lin, L. Zhou, T. Huang, and A. Yu, J. Mater. Chem. A, 1, 1239 (2013).
10. Y. Zhang, H. Zhang, J. Li, M. Wang, H. Nie, and F. Zhang, J. Power Sources, 240, 390 (2013).
11. J. Kang, O. Li, L. Li, and N. Saito, J. Power Sources, 261, 156 (2014).
12. J. Li, Y. Zhang, W. Zhou, H. Nie, and H. Zhang, J. Power Sources, 262, 29 (2014).
13. Z. Lyu, L. Yang, Y. Luan, X. Renshaw Wang, L. Wang, Z. Hu, J. Lu, S. Xiao, F. Zhang, X. Wang, F. Huo, W. Huang, Z. Hu, and W. Chen, Nano Energy, 36, 68 (2017).
14. Y. Tu, H. Li, D. Deng, J. Xiao, X. Cui, D. Ding, M. Chen, and X. Bao, Nano Energy, 30, 877 (2016).
15. Y. Lin, B. Moitoso, C. Martinez-Martinez, E. D. Walsh, S. D. Lacey, J.-W. Kim, L. Dai, L. Hu, and J. W. Connell, Nano Lett., 17, 3252 (2017).
16. J. Li, H. Zhang, Y. Zhang, M. Wang, F. Zhang, and H. Nie, Nanoscale, 5, 4647 (2013).
17. J. Ming, J.-B. Park, H.-S. Kim, C. S. Yoon, G. A. Eliau, B. Scrosati, Y.-K. Sun, and J. Hassoun, Solid State Ionics, 278, 133 (2015).
18. C. Tran, X. Q. Yang, and D. Qu, J. Power Sources, 195, 2057 (2010).
19. S. Meini, M. Piana, H. Beyer, J. Schwammlein, and H. A. Gasteiger, J. Electrochem. Soc., 159, A2135 (2012).
20. V. Y. Nimon, S. J. Visco, L. C. De Jonghe, Y. M. Volfovich, and D. A. Bograchev, ECS Electrochem. Lett., 2, A33 (2013).
21. M. Oliveras-Marin, P. Palomino, J. M. Amarilla, E. Enciso, and D. Tonti, J. Mater. Chem. A, 1, 14270 (2013).
22. S. B. Ma, D. J. Lee, V. Roev, D. Im, and S.-G. Doo, J. Power Sources, 244, 494 (2013).
23. C. N. Chervin, M. J. Wattendorf, J. W. Long, N. W. Kucko, and D. R. Rolison, J. Electrochem. Soc., 160, A1510 (2013).
24. N. Ding, S. W. Chien, T. A. Hor, R. Lum, Y. Zong, and Z. Liu, J. Mater. Chem. A, 2, 12433 (2014).
25. L. Ye, W. Lv, K. H. L. Zhang, X. Wang, P. Yan, J. H. Dickerson, and W. He, Energy, 83, 669 (2015).
26. L. Ye, X. Wang, W. Lv, J. Fei, G. Zhu, Y. Liang, Y. Song, J. Zhai, and W. He, Energy, 93, 416 (2015).
27. X. Li, L. Li, J. Huang, and A. Faghri, Energy, 81, 489 (2015).
28. I. Bardenhagen, M. Fenske, D. Fenske, A. Wittstock, and M. Bäumer, J. Power Sources, 299, 162 (2015).
29. H. D. Lim, H. Song, J. Kim, H. Gwon, Y. Bae, K. Y. Park, J. Hong, H. Kim, T. Kim, Y. H. Kim, X. Leprê, R. Ovaille-Robles, R. H. Baughman, and K. Kang, Angew. Chemie - Int. Ed., 53, 9216 (2014).
30. J. Xiao, D. Mei, X. Li, W. Xu, D. Wang, G. L. Graff, W. D. Bennett, Z. Nie, L. V Saraf, I. Aksay, J. Liu, and J.-G. Zhang, Nano Lett., 11, 5071 (2011).
31. Y. Cui and M. Zhang, ACS Appl. Mater. Interfaces, 5, 8173 (2013).
32. Y. Cui and M. Zhang, J. Mater. Chem. A, 1, 13984 (2013).
33. K. S. W. Sing, Pure Appl. Chem., 57, 603 (1985).
34. B. Sun, J. Zhang, P. Munroe, H.-J. Ahn, and G. Wang, Electrochem. commun., 31, 88 (2013).
35. P. Andrei, J. P. Zheng, M. Hendrickson, and E. J. Plichta, J. Electrochem. Soc., 157, A1287 (2010).
36. C. Xia, M. Waletzko, L. Chen, K. Peppler, P. J. Klur, and J. Janek, ACS Appl. Mater. Interfaces, 6, 12083 (2014).
37. B. Horstmann, B. Gallant, R. Mitchell, W. G. Bessler, Y. Shao-Horn, and M. Z. Bazant, J. Phys. Chem. Lett., 4, 4217 (2013).
38. R. R. Mitchell, B. M. Gallant, Y. Shao-Horn, and C. V. Thompson, J. Phys. Chem. Lett., 4, 1060 (2013).
39. V. Viswanathan, K. S. Thygesen, J. S. Hummelshøj, J. K. Nørskov, G. Girishkumar, B. D. McCloskey, and A. C. Luntz, J. Chem. Phys., 135 (2011).
40. Y. Yin, R. Zhao, Y. Deng, and A. A. Franco, J. Phys. Chem. Lett, 8, 599 (2017).
41. C. P. Andersen, H. Hu, G. Qiu, V. Kalra, and Y. Sun, J. Electrochem. Soc., 162, A1135 (2015).
42. C. Zhao, C. Yu, M. N. Banis, Q. Sun, M. Zhang, X. Li, Y. Liu, Y. Zhao, H. Huang, S. Li, X. Han, B. Xiao, Z. Song, R. Li, J. Qiu, and X. Sun, Nano Energy, 34, 399 (2017).
43. W. Fan, B. Wang, X. Guo, X. Kong, and J. Liu, Nano Energy, 27, 577 (2016).