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Nanoconfined growth of lithium-peroxide inside electrode pores: A noncatalytic strategy toward mitigating capacity-rechargeability trade-off in Lithium–Air battery

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Capacity-rechargeability trade-off in Lithium–Air battery remains as one of the major challenges before its practical realization. As the discharge capacity increases, an uncontrolled growth of lithium-peroxide leads to passivation of the conductive electrode by a thick insulating layer that limits charge transport and results in a high overpotential during recharge. In contrast, deposition of lithium-peroxide inside a spatially confined electrode-space can restrict the growth and improve the rechargeability of the cell. Small crystallite size of spatially confined lithium-peroxide inside porous framework is expected to show higher charge-transport that should play crucial role in its facile decomposition. Here, a prototypical approach shows how a controlled increase in pore diameter, pore volume and electrochemically active surface area of a mesoporous carbon produces much higher discharge capacity by improving mass diffusion inside the mesoporous channels, yet simultaneously achieves an efficient rechargeability due to pore-confinement of lithium-peroxide.

Introduction

Highest theoretical specific energy of 3.5 kWh kg⁻¹ makes Lithium–Air (Li–Air) battery as one of the most promising future energy storage technologies for both stationary and mobile applications. Ideally, the overall electrochemical reaction in a nonequilibrium Li–Air battery involves a two-electron (2e⁻) redox of oxygen (O₂) in the presence of lithium (Li⁺) ions (2Li⁺ + O₂ + 2e⁻ ↔ Li₂O₂(s); E° = 2.96 V vs. Li/Li⁺) leading to reversible formation (by the oxygen reduction reaction (ORR)) and decomposition (by the oxygen evolution reaction (OER)) of solid lithium peroxide (Li₂O₂) during discharge (DC) and recharge (RC), respectively.1 However, passivation of the conducting electrode by this ostensibly insulating solid Li₂O₂ layer (both ionic and electronic conductivities in the range of 10⁻¹⁸ to 10⁻²⁰ S cm⁻¹ at 25 °C) and diffusion-limitation of electroactive species in the electrode-pores result in lower than theoretically-predicted capacity, poor rechargeability, low rate capability etc.2-5 Although increase in carbon surface area as well as pore volume accessible to both O₂ and electrolyte could increase the DC capacity (QDC) of the cell, growth of large insulating crystals of Li₂O₂ with increase in QDC often led to deterioration of rechargeability as well as poor cyclability.6-8 The reason behind this low rechargeability is the limitation in charge transport through a thick Li₂O₂ layer that results in a high RC potential > 4 V vs. Li/Li⁺ and causes decomposition of both the nonaqueous

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A noncatalytic strategy toward mitigating capacity-rechargeability trade-off in Lithium–Air battery


effects to solve rechargeability problem in Li–Air battery by solid electrocatalysts could not truly improve the ORR/OER reversibility.11,12 Rather, the use of these “catalysts” exacerbated electrolyte/electrode instabilities. Furthermore, the soluble redox-mediators also seemed to have (in)stability issues and their use on an unprotected anode led to passivation of Li metal electrode.13,14 Therefore, it is necessary to identify a proper noncatalytic strategy to increase the capacity without sacrificing the rechargeability of a Li–Air battery.

Alternative to the usual uncontrolled growth of Li₂O₂ on widely used carbon nanotube (CNT) or carbon particle (Ketjen Black (KB), Super P (SP) etc.) based electrodes, confining the nucleation-and-growth of Li₂O₂ inside the framework-pores of a nanoporous carbon electrode can restrict the spatial growth of the discharge product below electron-tunnelling length and produce a nano-crystalline Li₂O₂ with small domain size. Compared to bulk crystalline Li₂O₂, this spatially-confined poorly crystalline Li₂O₂ with large interface with the carbon electrode is expected to show higher ionic and electronic conductivities that should suppress the recharge overpotential and help to achieve high round-trip energy efficiency in a Li–Air battery.15,16 However, at the same time it is necessary to ensure facile mass-transport and enough space inside the porous framework to produce large QDC in the cell. Subsequently, as a result of improved mass and charge transport due to nanoconfinement of Li₂O₂ in an electrode with sufficient porosity, high rate-capability during both DC and RC of the cell can also be achieved. Based on this idea, herein, we first confirm that compared to uncontrolled growth of Li₂O₂ on several commercial carbon electrodes, nanoconfinement of Li₂O₂ inside a mesoporous carbon results in a much higher round-trip energy efficiency (ratio of energy densities during DC and RC respectively) that does not deteriorate with increase in depth of
DC in a Li–Air battery. Further, we show that controlled increase in the electrochemically active surface area (ECSA), pore diameter and pore volume of the mesoporous carbon electrode gradually enhances $Q_{DC}$ by improving diffusion of electroactive species inside the mesoporous channels and simultaneously maintains an efficient rechargeability in a Li–Air battery due to decomposition of nanocrystalline Li$_2$O$_2$ confined inside discrete pores of the electrode. It has been found that proper optimization of the physico-chemical properties of the carbon electrode could achieve ~2.5 times improvement in $Q_{DC}$ but at the same time maintained an average RC potential of ~3.6 V vs. Li/Li$^+$ which is 400 to 700 mV lower than that of several other commercial carbon electrodes under similar conditions. This report demonstrates a prototypical strategy of a simple physico-chemical alteration in a porous carbon electrode as a metal-catalyst/promoter-free solution toward the capacity-rechargeability trade-off in Li–Air battery.

**Results and discussions**

**Effect of pore-confinement of Li$_2$O$_2$ in Li–Air cells.**

In order to verify the effect of pore-confined Li$_2$O$_2$ on suppressing RC overpotential ($\eta_{RC} = |E^0 - E_{RC}|$) we begin with comparing the DC/RC profiles of various carbon electrodes, such as CNT, KB, SP and mesoporous CMK-3, which have completely different surface morphologies and pore structures. While KB and SP carbons show particle-like morphology with 40-60 nm diameter, CNT has tubular morphology with an average outer diameter of 20-40 nm and length of 5-15 mm. The morphologies of these carbons are shown by the scanning electron microscopic (SEM) images in Figure S1 (a). Despite differences in morphologies, however, all these three commercial carbons give rise to inter-particle porosity with a random distribution of pore-space having diameter in the range of 50-100 nm. In contrast, CMK-3 with bead-like morphology has hexagonally ordered cylindrical mesopores (<4 nm diameter) aligned parallel to each other inside the carbon framework. Figure S1 (b) and (c) respectively show nitrogen adsorption/desorption isotherms measured at ~196 °C and pore-size distribution by Barrett-Joyner-Halenda (BJH) method for different carbons. The pore structures are schematically represented in Figure S1 (d). At first, DC/RC of the cells were carried out in dry air (maximum dew point < ~60 °C, < 11 ppm (v/v) H$_2$O) using 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in tetraethylene glycol dimethyl ether (TEGDME or tetraglyme; < 20 ppm H$_2$O) as the electrolyte up to a limited $Q_{DC}$ of 500 mAh g$^{-1}$ at the same DC/RC current density ($j_{DC/RC}$) of 100 mA g$^{-1}$. The galvanostatic DC/RC profiles in Figure 1 (a) show quite similar DC potentials for all the electrodes, but significantly different RC potentials. Among these carbons, the mesoporous CMK-3 electrode shows the lowest average RC potential of 3.6 V vs. Li/Li$^+$, whereas the same for SP, CNT and KB are 4.28, 4.17 and 3.98 V vs. Li/Li$^+$ respectively. Figure 1 (b) further shows that CMK-3 has the highest overall round-trip energy efficiency of 74% which is 7-14% higher than that of the other carbons. During DC in the non-mesoporous carbons the inter-particle void spaces get filled with a thick film-like crystalline Li$_2$O$_2$ (> 50 nm thick) that has very poor ionic as well as electronic conductivities and as a result, the decomposition of this insulating Li$_2$O$_2$ on these non-mesoporous carbons requires very high $\eta_{RC}$ (usually, $\eta_{RC} > 1$ V). On the other side, the low $\eta_{RC}$ in CMK-3 electrode can certainly be corroborated to facile decomposition of nanoconfined Li$_2$O$_2$ inside the mesoporous channels having average pore diameter of 3.6 nm (see later).

**Figure 1.** (a) Galvanostatic discharge (DC)/recharge (RC) profiles of Li–Air cells with different carbon electrodes in 1 M LiTFSI/tetraglyme electrolyte up to a fixed capacity of 500 mAh g$^{-1}$ at the same current density of 100 mA g$^{-1}$. (b) Comparison of round-trip efficiencies calculated from the ratio of energy densities during DC and RC respectively for the Li–Air cells with different electrodes. Schematic representation of Li$_2$O$_2$ deposition (shown in blue) inside (c) KB/SP, (d) CNT and (e) CMK-3 electrodes.
The spatially restricted growth keeps the thickness of Li$_2$O$_2$ well below the electron tunneling limits (~10 nm) and the small crystallite size results in much higher ionic conductivity compared to crystalline Li$_2$O$_2$.\cite{2,15} Therefore, circumvention of charge-transport-limitation by nanofineannealing of Li$_2$O$_2$ should be a definite reason behind the suppression of $\eta_{DC}$ in CMK-3 electrode. The deposition of Li$_2$O$_2$ in these carbon electrodes is shown by the SEM images in Figure S1 (e) and is schematically represented in Figure 1 (c-e). In order to verify the possibility of mass diffusion inside the mesoporous channels of CMK-3, we have precisely determined the hydrodynamic radii of the electroactive species in the electrolyte by using Stokes-Einstein equation

$$D = \frac{k_B T}{6 \pi \mu r}$$

where $D$, $k_B$, $T$, $\mu$ and $r$ are the diffusion coefficient of the electroactive species, Boltzmann constant, temperature, viscosity of the electrolyte and hydrodynamic radius of the electroactive species in the electrolyte solution, respectively. The hydrodynamic radii of oxygen, Li$^+$ and TFSI$^-$ species in 1 M LiTFSI/tetraglyme solution under air atmosphere (~0.21 bar O$_2$) are calculated to be ~1.2, 0.41 and 0.28 nm, respectively and the detailed information with the values of all parameters used in this calculation are provided in Supporting information. These results confirm that the electroactive species can permeate through the porous channels of the CMK-3 electrode and take part in the electrochemical reactions inside the confined pore-space. However, it should be noted that although the hydrodynamic radii of the electroactive species are smaller than the radii of the mesopores in CMK-3 and additional capillary forces help O$_2$ and electrolyte solution to diffuse into the mesoporous channels, the deposition of solid Li$_2$O$_2$ continuously decreases the porosity and blocks the diffusion channels during DC.\cite{18,19} As a result, the CMK-3 electrode shows much lower Q$_{DC}$ (827 mAh g$^{-1}$) than that calculated (1920 mAh g$^{-1}$) from full utilization of the mesopore volume (0.71 cm$^3$ g$^{-1}$) (see later). Nonetheless, oxygen diffusion limitation is a general problem in air-electrodes, which are quite sensitive to the (1920 mAh g$^{-1}$) and a significantly lower 4.5 V cut-off conditions of 2–6 · 13% higher than that of other carbons under air atmosphere for a full DC up to 2 V vs. Li/Li$^+$ and the results are shown in Figure S2 (d). Owing to this high rechargeability, therefore, an efficient way has to be found out to further enhance the Q$_{DC}$ of the mesoporous electrode toward mitigating the capacity-rechargeability trade-off in Li–Air cells. In order to enhance the Q$_{DC}$ of the mesoporous electrode, we adopted two different strategies: one of these was to induce solution mediated DC, while the other was to strategically modify the porosity of the carbon to enhance mass diffusion inside the porous framework.

**Promoter assisted increase in Q$_{DC}$ of mesoporous electrode.**

Lithium nitrate (LiNO$_3$) and 2,5-di-tert-butyl-1,4-benzoquinone (DBBQ) were considered as the two promoters to induce solution mediated growth of Li$_2$O$_2$ and to increase the Q$_{DC}$ of CMK-3 electrodes.\cite{20,21} Specifically, we used 1 M LiNO$_3$ in tetraglyme and 1 M LiTFSI + 50 mM DBBQ in tetraglyme as the two electrolytes in Li–Air cells. Figure 2 (a) shows the full DC/RC curves of CMK-3 electrodes in different electrolytes with or without promoters under dry air with the cut-off conditions of 2–4.5 V vs. Li/Li$^+$ at $j_{DC/RC}$ of 100 mA g$^{-1}$. It is indeed found that the use of LiNO$_3$ and addition of DBBQ to LiTFSI as a promoter significantly increase the Q$_{DC}$ of CMK-3 electrodes. A quantitative comparison of Q$_{DC}$ in different electrolytes in Figure 2 (b) demonstrates that the Q$_{DC}$ of CMK-3 increases from 827 mAh g$^{-1}$ in 1 M LiTFSI to 1319 mAh g$^{-1}$ in 1 M LiNO$_3$ and 1863 mAh g$^{-1}$ in 1 M LiTFSI + 50 mM DBBQ in tetraglyme electrolyte. However, this gain in Q$_{DC}$ due to enhanced solution mediated deposition of Li$_2$O$_2$ is achieved at the cost of round-trip efficiency of the cells. From Figure 2 (b), the round-trip efficiency of ~73% in 1 M LiTFSI decreases to ~67% in 1 M LiNO$_3$ and ~50% in 1 M LiTFSI + 50 mM DBBQ in tetraglyme electrolyte. The X-ray diffraction (XRD) patterns in Figure S3 (a) confirm the formation of Li$_2$O$_2$ as the discharge product in all these three electrolytes and a detailed analysis of the XRD data in Figure S3 (b) shows a slight increase in domain size for the (100) reflection and an anisotropic growth of Li$_2$O$_2$ crystals with enhanced solution mediated DC of CMK-3 electrode. Since occurrence of parasitic side reactions is thought to be a reason of poor rechargeability, we have also quantified the discharged Li$_2$O$_2$ by titration with TiOSO$_4$ solution.\cite{9} A much lower than 100% yield of Li$_2$O$_2$ after DC definitely indicates occurrence of parasitic side reactions during DC. However, the Li$_2$O$_2$ yields of 71±2, 74±1 and 67±2% in 1 M LiTFSI, 1 M LiNO$_3$ and 1 M LiTFSI + 50 mM DBBQ in tetraglyme.
efficient ORR catalysts that showed higher adsorption energies for
previously demonstrated the activities of N-doped carbons as inside the porous structure for higher
diameter, pore volume, ECSA and number of ORR active sites
2
2
In contrast to promoter assisted uncontrolled growth of Li
Modification of mesoporous carbon for improved mass diffusion.
result, solution mediated increase in can be attributed to thicker Li
3
2
2
O2
2
LNO
2
LiTFSI+DBBQ
LITFSI
Q (mAh g⁻¹)
500 1000 1500 2000
75 70 67 65 60 55 50 45
(b)
QDC (mAh g⁻¹)
Round-trip eff. (%)
400.5±0.3 and 403.8±0.3 eV, corresponding to pyridinic,
Deconvoluted N1s XPS show three characteristics peaks at
XPS of all the carbon materials are shown in Figure S6 (a-d) and the
functionalities, we carried out X-ray photoelectron spectroscopic
(EDS) identifying the surface
labelled as N-CMK-3-1 to -4 in the increasing order of N-content. The
synthesized four different N-doped CMK-3 carbons which are
as the carbon source. By changing the concentration of urea, we
templating route using phenol-urea-formaldehyde (PUF) precursor
relative ease of synthesis, we synthesized N-doped CMK-3 by a hard-
N30
1. In all cases the N
respectively and the corresponding values are summarized in Table
BJH pore size distributions are shown in Figure S7 (a) and (b)
Halenda (BJH) method. The adsorption/desorption isotherms and
196
(876) 888
1.0, 0.45–0.55, indicating presence
of N-CMK-3 samples evinces the presence of quite complex
Furthermore, the H2(b) hysteresis in the isotherms
pore size analysis also shows a narrow pore-size distribution with a
sharp peak at 3.6 nm. Similar type IV isotherms are observed for all
P/B0
0.45–0.55, indicating presence of high pore-size uniformity in the framework mesopores.31 The BJH pore size analysis also shows a narrow pore-size distribution with a sharp peak at 3.6 nm. Similar type IV isotherms are observed for all the N-CMK-3 samples except that the capillary condensation takes place at higher P/P0 (> 0.6), which indicates the presence of larger mesopores since capillary condensation pressure is a function of pore diameter.
4
Furthermore, the H2(b) hysteresis in the isotherms of N-CMK-3 samples evinces the presence of quite complex
Au, Pd and Ru) and transition-metal oxide (MnO2, MnO, CoO, etc.)
catalysts, N-doped carbons are attractive due to low-cost, high
electronic conductivity and large surface area. Besides, several N-
doped mesoporous carbons were reported to possess bimodal
porosity with larger mesopores that can improve mass diffusion
during operation of Li–Air cells.27, 28 For these reasons, and due to
relative ease of synthesis, we synthesized N-doped CMK-3 by a hard-
templating route using phenol-urea-formaldehyde (PUF) precursor
as the carbon source. By changing the concentration of urea, we
synthesized four different N-doped CMK-3 carbons which are
labelled as N-CMK-3-1 to -4 in the increasing order of N-content. The
SEM images of the undoped and N-doped CMK-3 samples showing bulk morphologies and the corresponding elemental mapping by
energy dispersive X-ray spectroscopy (EDS) identifying the surface
chemical compositions are demonstrated in Figure S5 (a-e). The SEM images show similar morphologies of the CMK-3 and N-CMK-3 samples, whereas the EDS mapping of the N-doped samples confirms
quite well dispersed doping of nitrogen in the carbon structure. In
to nitrogen, high content of oxygen functionalities is also observed
in all the carbon samples. In order to provide a quantitative idea about N-doping and to precisely identify the N and O-
funktionalities, we carried out X-ray photoelectron spectroscopic
(XPS) analyses of all the samples. The wide-scan, O1s, N1s and C1s
XPS of all the carbon materials are shown in Figure S6 (a-d) and the
N/C and O/C values of all the samples are tabulated in Table 1. Deconvoluted N1s XPS show three characteristics peaks at
398.5±0.2, 400.5±0.3 and 403.8±0.3 eV, corresponding to pyridinic,
pyrrolic and oxidized nitrogen, respectively, as shown in Figure S6
(c).27 The O1s and C1s XPS of all the samples in Figure S6 (b) and (d),
respectively, identify C–O (e.g., phenol, ether, epoxy etc. at C1s
~286.8±0.3 eV and O1s ~532.5±0.1 eV), C=O (e.g., carbonyl, quinone
etc. at C1s 287.7±0.3 eV and O1s 530.5±0.2 eV) and –COO⁻ (e.g.,
carboxylic acid, ester, lactone etc. at C1s 289.3 eV) groups to be
present as the oxygen functionalities.29 The oxygen present in
phenol, formaldehyde and urea are thought to be the sources of
these oxygen functionalities in the carbon. The specific surface area
(SBET) of all the samples was evaluated by Brunauer-Emmett-Teller
(BET) method from the N2 adsorption/desorption data obtained at
196 °C and the pore structure was analyzed by Barrett-Joyner-
Halenda (BJH) method. The adsorption/desorption isotherms and
BJH pore size distributions are shown in Figure S7 (a) and (b)
respectively and the corresponding values are summarized in Table
1. In all cases the N2 adsorption/desorption shows a type IV isotherm
which is the characteristic of a mesoporous material.30 In case of
CMK-3, a steep N2 adsorption (capillary condensation) takes place in
the relative pressure (P/P0) range of 0.45–0.55, indicating presence
of high pore-size uniformity in the framework mesopores.31 The BJH pore size analysis also shows a narrow pore-size distribution with a
sharp peak at 3.6 nm. Similar type IV isotherms are observed for all
the N-CMK-3 samples except that the capillary condensation takes
place at higher P/P0 (> 0.6), which indicates the presence of larger
mesopores since capillary condensation pressure is a function of
pore diameter.30 Furthermore, the H2(b) hysteresis in the isotherms
of N-CMK-3 samples evinces the presence of quite complex
Modification of mesoporous carbon for improved mass diffusion.
In contrast to promoter assisted uncontrolled growth of Li2O2,
modification of the mesoporous carbon in terms of increase in the
pore diameter, pore volume, ECSA and number of ORR active sites
should be a better alternative not only to improve mass diffusion
inside the porous structure for higher QDC but also to maintain a
controlled and restrictive growth of Li2O2 for facile decomposition
during RC. Several experimental and theoretical studies have
previously demonstrated the activities of N-doped carbons as
efficient ORR catalysts that showed higher adsorption energies for
both lithium and oxygen and facilitated the nucleation of Li2O2 on
the electrode-surface.24,26 Furthermore, compared to precious metal (Pt,
interconnected ink-bottle-shaped pore networks with a narrow distribution of pore bodies but a wide neck size distribution.\textsuperscript{32, 33} From the BJH pore size analysis it is indeed found that the N-CMK-3 carbons show bimodal porosity and as the N-content increases in the carbon framework, the pore diameter gradually increases and becomes more distributed. Since the samples were synthesized using mesoporous SBA-15 silica as the template, ideally the predominant pore diameter of all the samples should be very close to the wall thickness of the SBA-15 (~ 4.5 nm). But, due to shrinkage of the pores in the carbon framework during carbonization of the precursor and template-removal steps, the pore diameter (3.6 nm) of the CMK-3 becomes lower than the pore wall thickness of the SBA-15 template. In contrast, the presence of larger mesopores (diameter ~ 6 nm) and ink-bottle-like cavities in the N-doped carbons can be explained by incomplete filling of PUF precursors inside SBA-15 template during synthesis and partial decomposition of PUF polymer during carbonization process, leaving empty space in the carbon backbone. The CMK-3 was synthesized by polymerization of phenol-formaldehyde (PF) mixture and subsequent carbonization of the PF resin. In contrast, for the synthesis of N-CMK-3 samples PUF precursor was used, where there are possibilities of several individual reactions, such as addition and condensation reactions of phenol, urea, and formaldehyde.\textsuperscript{34} Therefore, different self-condensation and co-condensation products can be formed during polymerization of the PUF precursor. This difference in polymerization process can affect the filling level of the SBA-15 template and produce cavities in the resulting N-doped carbons. Furthermore, addition of urea to PF resin results in poor bonding strength and lowers the stability of the resin that can decompose as well as shrink during the carbonization process.\textsuperscript{35} As a result, the N-CMK-3 samples show larger and more distributed mesopores compared to the CMK-3 carbon. Consequently, due to this enlargement of pore diameter and formation of interconnected framework cavities, the N-CMK-3 samples exhibit higher pore volume (\(V_{\text{m}}\)) and the values are shown in Table 1. The mesoporous structure of the samples was visualized by transmission electron microscopic (TEM) images which, in Figure 3 (a-e), clearly demonstrate a hexagonally ordered mesopore arrangement for all the samples. Summarizing all these results, it is seen that N-doping of CMK-3 by addition of urea as a precursor not only increases the number of ORR active sites, but also successfully increases the porosity that can be further beneficial for Li–Air battery operations. A schematic representation of the synthetic procedure of the mesoporous carbons is shown in Figure 3 (f).

Discharge of N-CMK-3 electrodes in Li–Air cells.

All the CMK-3 and N-CMK-3 electrodes were discharged and recharged in 1 M LiTFSI/tetraglyme electrolyte (< 20 ppm H\textsubscript{2}O) under dry air with the cut-off condition of 2–4.5 V vs. Li/Li\textsuperscript{+} at \(i_{\text{DC/RC}}\) of 100 mA g\textsuperscript{-1}. Figure 4 (a) shows the galvanostatic DC/RC curves of the undoped and doped CMK-3 electrodes. At a glance, the galvanostatic results demonstrate that N-doping of CMK-3 significantly increases the \(Q_{\text{DC}}\) of the cells. From the quantitative comparison of \(Q_{\text{DC}}\) of doped and undoped CMK-3 electrodes in Figure 4 (b) it is found that with increase in N/C atomic ratio, the \(Q_{\text{DC}}\) of the mesoporous carbon gradually increases from 827 mAh g\textsuperscript{-1} in CMK-3 (N/C= 0) to 1385 (N-CMK-3-3, N/C= 0.029), 1528 (N-CMK-3-2, N/C= 0.032) and 2111 mAh g\textsuperscript{-1} (N-CMK-3-3, N/C= 0.04) before decreasing to 1668 mAh g\textsuperscript{-1} in N-CMK-3-4 (N/C= 0.051). Interestingly, the values of \(Q_{\text{DC}}\) do not follow the trend of N/C ratio and the peak of \(Q_{\text{DC}}\) at 2111 mAh g\textsuperscript{-1} for N-CMK-3-3 and then decrease in the value to 1668 mAh g\textsuperscript{-1} for N-CMK-3-4 certainly indicate that increase in concentration of nitrogen as the ORR active sites is not the sole reason for capacity enhancement in these N-doped CMK-3 electrodes. In order to understand the reason behind the increase in \(Q_{\text{DC}}\) upon N-doping of CMK-3 electrode, we thoroughly analyzed the pore structures of these carbon materials. Figure 4 (c) shows a decreasing trend of the \(S_{\text{BET}}\) with increase in N/C ratio. Surprisingly this observation is contradictory to the trend of \(Q_{\text{DC}}\) for these electrodes because intuitively, capacity should be proportional to the surface area of the electrodes. Nonetheless, the pore size and pore volume of these carbons seem consistent with \(Q_{\text{DC}}\) values.

Figure 3. Transmission electron microscopy (TEM) images of (a) CMK-3, (b) N-CMK-3-1, (c) N-CMK-3-2, (d) N-CMK-3-3 and (e) N-CMK-3-4. (f) Schematic representation of the synthetic steps for the mesoporous carbons.
Table 1. Physico-chemical properties of mesoporous carbons

|              | N/C | O/C | $S_{\text{BET}}$ ($\text{m}^2\text{g}^{-1}$) | $V_{\text{BJH}}$ ($\text{cm}^3\text{g}^{-1}$) | ECSA ($\text{m}^2\text{g}^{-1}$) |
|--------------|-----|-----|---------------------------------|---------------------------------|-------------------------------|
| CMK-3        | 0   | 0.093 | 1083                           | 0.71                            | 20.7                          |
| N-CMK-3-1    | 0.029 | 0.072 | 1052                           | 1.08                            | 26.4                          |
| N-CMK-3-2    | 0.032 | 0.091 | 1040                           | 1.12                            | 27.2                          |
| N-CMK-3-3    | 0.04  | 0.087 | 1013                           | 1.18                            | 28.3                          |
| N-CMK-3-4    | 0.051 | 0.09 | 898                            | 1.12                            | 23.9                          |

Increase in the pore diameter from 3.7 to ~ 6 nm is certainly expected to enhance mass transport inside the N-CMK-3 electrodes compared to undoped CMK-3. Furthermore, as shown in Figure 4 (c), with increase in N/C atomic ratio, the pore volume gradually increases, reaches at peak for N-CMK-3-3 (1.18 cm$^3$ g$^{-1}$, N/C of 0.04) with 66% enhancement from the undoped one (0.71 cm$^3$ g$^{-1}$, N/C of 0) and then decreases for N-CMK-3-4 (1.12 cm$^3$ g$^{-1}$, N/C of 0.051) electrode. As mentioned earlier, during synthesis of these carbons, different filling levels of the pores of SBA-15 template by the precursors and partial decomposition of PUF resin with relatively low mechanical strength result in higher pore volume in N-CMK-3 samples compared to the undoped CMK-3. However, too high fraction of urea for the synthesis of N-CMK-3-4 (urea to phenol ratio of 1.06) might have lowered the mechanical strength of the precursor resin excessively and possible occurrence of several self and co-condensation reactions producing small fragments instead of continuous polymeric
network could lead to partial collapse of the carbon framework during carbonization. As a result, N-CMK-3-4 breaks the increasing trend of pore volume with N/C ratio and shows smaller pore volume compared to N-CMK-3-3. Since ECSA provides a more precise estimate of the electrode-area available for electrochemical reactions, we measured and plotted the ECSA (see Supporting information for detailed calculation) of these mesoporous carbons in Figure 4 (c). Interestingly, the ECSA values do not follow the trend of $S_\text{BET}$, rather show the similar trend of pore volume and correlate with the observed $Q_{\text{OC}}$ of the electrodes. This correlation can be attributed to enhanced penetration of electroactive species inside the mesoporous framework as the pore diameter and pore volume of the carbon increase. After DC of the cells in air the discharged electrodes were thoroughly analyzed by XPS, infra-red spectroscopy (FTIR) and XRD to identify the predominant DC products. Figure S8 (a-b) shows XPS of discharged CMK-3 and N-CMK-3-3 electrodes, respectively. The single component Li1s spectra at ~ 55 eV and O1s spectra at ~ 532 eV confirm the deposition of Li2O2 as the major DC product. Besides, The O1s spectra show additional peaks at > 532 eV that can be assigned to –COOH, –CO or SO2 species resulting from parasitic reactions or adsorbed electrolyte residues on the deposited Li2O2 and additionally multiple components in the deconvoluted C1s spectra also indicate presence of several functionalities, such as C–C, CHx, CO2 etc., in the discharged electrodes. Consistent with the XPS results, the FTIR spectra of the discharged CMK-3 and N-CMK-3-3 electrodes in Figure S9 identify Li2CO3 and Li-carboxylates to be the parasitic products during DC. There can be different ways for the formation of parasitic side products in Li–Air cells where, in addition to electrolyte and electrode decomposition, the CO2 (0.04%) present in air can also undergo electrochemical reaction during DC to directly produce Li2CO3 as an undesired product. Nevertheless, parasitic side reaction between the carbon electrode as well as the nonaqueous electrolyte with superoxide intermediate is a persistent problem in Li–Air battery that demands for more stable electrolytes and electrode materials. Figure 4 (d) and Figure S10 show the XRD patterns of the discharged CMK-3 and N-CMK-3 electrodes. These XRD patterns not only confirm Li2O2 as the DC product in these electrodes, but also show significant decrease in peak intensity in high N/C ratio in the N-doped carbons. This means lower fractions of crystalline Li2O2 are deposited as the N/C ratio increases. Besides, a gradual broadening of both (100) and (101) reflections of Li2O2 is observed with increase in N/C ratio. The broadening of the XRD peaks indicates a decrease in the average Li2O2 crystallite-size which is plotted in Figure 4 (e) for all the samples. It is found that the respective crystallite size for the (100) and (101) reflections of Li2O2 decreases from ~ 8 and 7.7 nm in CMK-3 to ~ 6.1 and 4.1 nm in N-CMK-3-4. Unlike unrestricted growth of Li2O2 crystals in conventional carbons without framework-porosity, here in these cases of mesoporous carbons the initial nucleation takes place inside a confined porous channel that restricts the spatial growth of Li2O2. As shown earlier in this article, the hydrodynamic radii of the electroactive species are much smaller than that of the mesopores in these N-doped carbons. Furthermore, the interconnected ink-bottle pores in N-CMK-3 electrodes are expected to show more facile mass transport along the mesoporous channels. Once diffuse into the pores, these electroactive species get confined inside the nanoscopic space where heterogeneous interaction between the reactants and the electrode surface is tremendously amplified. Consequently, very high interfacial area inside the mesopores significantly enhances the kinetics of the electrochemical reactions. Moreover, turbostratic structure with considerable defects and N/O-doping enhance the ORR activity in these mesoporous CMK-3 based materials compared to other commercial carbons. We have compared the ORR activities of all the CMK-3 and N-CMK-3 electrodes by a cathodic linear sweep voltammetry (LSV) in the range 3.2 to 2 V vs. Li/Li+ at a sweep rate of 0.5 mV s⁻¹ using metallic Li as both the counter and reference electrodes. Apparently, the integrated areas under the LSV curves in Figure S11 (a) depicting the amount of charge passed for ORR show similar trend of $Q_{\text{OC}}$ observed in galvanostatic DC. Figure S11 (b) shows the current densities ($j_\text{ORR}$) of all these electrodes at three different potentials of 2.8, 2.7 and 2.6 V vs. Li/Li+ during LSV scan, where overall a gradual increase in ORR current response has been observed with increase in N/C ratio in the N-CMK-3 electrodes. We have also identified the overpotential ($\eta = | 2.96 – E |$, V) required to reach the $j_\text{ORR}$ of 0.05, 0.1 and 0.15 mA cm⁻² in all these undoped and N-doped CMK-3 electrodes and the results in Figure S11 (c) consistently show that with increase in N/C ratio the overpotential to reach respective $j_\text{ORR}$ becomes lower. Furthermore, the Tafel plots in Figure S11 (d) yield Tafel slopes of 473, 370, 383, 373 and 443 mV dec⁻¹ for CMK-3 and N-CMK-3-1 to -4 electrodes respectively and these values unequivocally demonstrate an enhancement in ORR activities of the N-CMK-3 electrodes compared to the undoped one. As a result of this good electrocatalytic activity, the strong interaction between depositing Li2O2 and the surface of the N-doped electrode leads to growth of a poorly crystalline thin-film-like Li2O2 on the surface of the carbons, even outside of the porous framework (SEM in Figure S12). Therefore, despite higher $Q_{\text{OC}}$ in N-CMK-3 electrodes, owing to the structural effect of the porous framework as well as the electrocatalytic activities of the N-sites, the size of individual Li2O2 crystallites remains small. It is important to note from Figure 4 (a) and (b) that the increase in $Q_{\text{OC}}$ in the case of N-CMK-3 electrodes does not affect the rechargeability and overall round-trip efficiency of the cells. The average RC potential for all the CMK-3 and N-CMK-3 electrodes has been calculated to be $< 3.65$ V vs. Li/Li+ and Figure 4 (b) shows that > 70% round-trip efficiency is maintained in all the N-doped electrodes despite up to ~ 2.5 times increase in $Q_{\text{OC}}$ during full DC/RC in air. These results demonstrate a successful mitigation of capacity-rechargeability trade-off in Li–Air battery. A closer look at the galvanostatic curves reveals that the RC at these electrodes starts at potentials very close to 3 V vs. Li/Li+, remains below 3.5 V vs. Li/Li+ up to 50% state of charge (SOC) and goes above 4 V vs. Li/Li+ at 70-75% SOC. Online electrochemical mass spectrometry (OEMS) of N-CMK-3-3 as the representative electrode shows the trend of gas evolution during RC of a cell with N-doped mesoporous carbon. Correlating the RC curve of N-CMK-3-3 in Figure 5 (a) with OEMS data in Figure 5 (b)
it is found that O₂ gas starts evolving as soon as RC of the cell begins and O₂ evolution is very close to 3 V vs. Li/Li⁺. The gas evolution trend further shows that as the RC progresses, copious amount of O₂ is evolved below 3.5 V vs. Li/Li⁺. These observations give direct evidence of a facile decomposition of Li₂O₂ below 3.5 V vs. Li/Li⁺ in case of N-CMK-3-3 electrode. However, gradual increase in RC potential and large amount of carbon dioxide (CO₂) evolution at the later part of RC (> 4 V vs. Li/Li⁺) indicate decomposition of deposited parasitic side products, such as lithium carbonate and lithium carboxylate, as evidenced by XPS and FTIR observations. Nevertheless, when compared with OEMS data of CNT electrode in Figure S13 (a) and (b), this mesoporous N-CMK-3-3 electrode shows much better O₂ evolution efficiency and lower amount of evolved CO₂. In CNT electrode, the onset potential for O₂ evolution is > 3.5 V vs. Li/Li⁺ and a significant flux of O₂ is achieved only at potentials > 4 V vs. Li/Li⁺. These comparative results definitely confirm the efficiency of N-doped mesoporous carbons for the facile decomposition of Li₂O₂ during RC of the cell. Interestingly, the efficacy of O₂ evolution by the decomposition of Li₂O₂ seems quite similar for N-CMK-3-3 and CMK-3 electrodes, as shown in Figure S14 (a) and (b). These similarly efficient O₂ evolution efficiencies of N-CMK-3-3 and CMK-3 electrodes reaffirm the role of mesopores for facile decomposition of Li₂O₂. However, at the same time it indicates no additional contribution from N-sites as an OER catalyst during RC of the cells. In order to ascertain OER catalytic activity trend with N/C ratio, we have carried out anodic LSV (0.05 mV s⁻¹) of these electrodes after reduction up to QDC of 0.5 mAh cm⁻² as shown in Figure S15 (a) that exhibits two pronounced oxidation peaks, one centered around 3.4 V vs. Li/Li⁺ and another above 4 V vs. Li/Li⁺. In order to compare the OER activities of these electrodes, we have analyzed the LSV curves in the QNC range below 250 mV. The onset potentials for OER of all the mesoporous electrodes are found to be quite similar and close to 3 V vs. Li/Li⁺. However, interestingly, the current responses at different overpotentials (see Figure S15 (b)) and vice versa (see Figure S15 (c)) do not show any correlation with N/C ratio. Therefore, the direct role of N-sites for catalyzing OER cannot be confirmed in these electrodes. Rather, these results evince the predominant effect of nanoconfined Li₂O₂ in suppressing ηNC of the cells. Although Li₂O₂ is thought to be a wide-bandgap insulator (band gaps of 5–6.4 eV), electrochemically formed Li₂O₂ usually possesses several defect sites that act as the charge carriers and improve the overall conductivity. Specifically, in case of mesoporous electrodes, nanocrystalline Li₂O₂ with large number of defect-rich interfaces and grain boundaries may play significant role in enhancing the charge carrier dynamics that should benefit a facile decomposition during RC of the cells. Moreover, according to density functional theory (DFT) calculations, cohesive interactions of Li and O₂ with carbon surface during nucleation of Li₂O₂ lead to electron transfer from the anti-bonding O₂ orbitals to the carbon electrode and induce a p-type conductivity at Li₂O₂/electrode interface. As a result of the strong interaction with carbon, the Li–O bond length in the nucleating Li₂O₂ may also elongate and diminish the interaction between Li and O atoms resulting in higher mobility of Li⁺ in the Li₂O₂ crystal. A comparative impedance analysis of discharged KB and N-CMK-3-3 electrodes in Figure S16 indeed shows more facile charge transport for the latter electrode and supports the hypothesis presented in this work. In case of N and O-doped carbons, the electron-withdrawing hetero atoms can activate neighboring C atoms for stronger adsorption of Li and O₂ and induce deposition of disordered or poorly-crystalline Li₂O₂ as the discharged product, which is consistent with the XRD results in Figure 4 (d) and (e). A prior DFT calculation showed that during DC of the cell the binding of depositing Li₂O₂ units on top of the initially nucleated disordered Li₂O₂ layer becomes weak with lower than expected coordination number and continues building up disordered structure. Therefore, in the cases of N-CMK-3 electrodes depositions of the poorly crystalline Li₂O₂ having weaker bonding, lower coordination number and improved ionic/electronic conductivities continue despite increase in QNC and maintain low ηNC during RC of the cells.

Comparison of rate capabilities of different electrodes in Li–Air cells.

Retention of high QDC together with low ηNC at high current densities is significantly important for the development of practical Li–Air batteries. Figure S17 (a)-(d) respectively show the galvanostatic DC/RC curves of Li–Air cells with N-CMK-3-3, KB, CNT and SP electrodes at different jDC from 100 to 500 mA g⁻¹. From these DC/RC curves, we have calculated and compared the gravimetric energy and power densities of these electrodes during DC and the results are shown by the Ragone plots in Figure 6 (a). Expectedly, all the electrodes show an apparent anticorrelation between gravimetric energy and power capabilities due to charge transport as well as oxygen diffusion limitations at high jDC. Build-up of an insulating Li₂O₂ layer during DC increases the electronic resistivity of the carbon electrode and at the same time blocks the oxygen diffusion paths resulting in lower QDC at higher jDC. Nonetheless,
Among these carbon electrodes, N-CMK-3-3 and KB show much better retention of gravimetric energy at high power compared to the other two electrodes. Higher surface area (both $S_{BET}$ and ECSA) and pore volume of N-CMK-3-3 and KB than those of CNT and SP can be attributed to this higher energy and power capabilities. Therefore, consistent with previous report, high surface area and large pore volume in a carbon electrode seem to be essential requirements to achieve simultaneously high energy and power densities during DC of a Li–Air battery. However, Figure 6 (b) shows that the trend of DC performances in these electrodes does not correlate to the rechargeability of the cell. Considering rechargeability, the performance of N-CMK-3-3 profoundly stands out from the other three electrodes. The N-CMK-3-3 electrode consistently maintains a round-trip energy efficiency of > 70% at high $j_{DC}$ up to 500 mA g$^{-1}$, which is 5-15% higher than those of KB, CNT and SP. This significantly higher rechargeability of N-CMK-3-3 electrode at high rate can again be ascribed to the formation of spatially restricted poorly crystalline Li$_2$O$_2$ with better Li$^+$ mobilities that can transport charges more rapidly compared to bulk crystalline Li$_2$O$_2$ formed in other electrodes. These results indicate that high surface area and large pore volume coupled with mesoporous framework help N-CMK-3-3 electrode to produce high capacity with efficient rechargeability even at high current rates during both DC and RC, respectively. The efficient rechargeability of N-CMK-3-3 electrode was tested over repeated cycles and was also compared with the cyclability of KB electrode under same conditions and the results are shown in Figure S18. The cycling data further show better performance for the N-CMK-3-3 electrode in suppressing the $\Delta n_{sc}$ over several cycles. However, deterioration in cycling stability is evident for both these electrodes and this can be attributed to parasitic side reactions as explained before.

**Conclusion**

In summary, we have successfully demonstrated a noncatalytic strategy to improve the discharge capacity of a Li–Air battery without sacrificing the rechargeability and overall energy efficiency of the cell. To do so, we have chosen a mesoporous carbon as the electrode material that offers a confined pore-space for spatially restricted growth of Li$_2$O$_2$. Unlike uncontrolled growth of Li$_2$O$_2$ in conventional high surface area electrodes, the confined growth inside the mesoporous produces nano-structured Li$_2$O$_2$ that is benefited with high mobility of Li$^+$ and other charge carriers for facile decomposition during recharge. We have further shown that controlled increase in electrochemically active surface area, pore width and pore volume of the carbon, while maintaining the mesoporous framework, can significantly enhance the discharge capacity and at the same time retains high rechargeability. In our study, we followed a wet chemical pathway for the synthesis of mesoporous carbons using mesoporous silica as the hard template that was impregnated with phenol-formaldehyde mixture with or without urea as the carbon precursor. Our results have shown that addition of urea not only introduces nitrogen as a dopant in the carbon skeleton but also increases the porosity in the framework. For a certain dopant concentration, the porosity reaches a maximum and the electrode produces a discharge capacity that is nearly 2.5 times higher than that of the undoped carbon. Interestingly, despite this significant increase in discharge capacity, the electrode still maintains a round-trip energy efficiency of > 70% which is up to 15% higher than that in the conventional electrodes. Detailed investigations have found that, although enhanced porosity accommodates larger amount of Li$_2$O$_2$ and gives higher discharge capacity, the mesoporous framework in the N-doped carbons produces spatially-restricted nano-sized and poorly crystalline Li$_2$O$_2$ that decomposes at low recharge potential. Our study demonstrates a prototypical strategy of electrode modification for controlled growth of Li$_2$O$_2$ in order to achieve high capacity with simultaneously high rechargeability and provides crucial insights into electrode design for future development of efficient Li–Air batteries.

**Author contributions**

A. D. conceived the research, synthesized the materials, carried out the electrochemical measurements and wrote the manuscript. K. I. carried out the OEMS experiments and Y. K. supervised the overall research and contributed to scientific discussions and writing of the manuscript.
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Conflicts of interest
The authors declare no conflict of interest.

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