Electrochemical properties of graphene flakes as an air cathode material for Li–O₂ batteries in an ether-based electrolyte†

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We employed graphene flakes as an air-cathode material for Li–O₂ batteries and investigated their electrochemical properties in the dimethyl ether electrolyte. Graphene flakes were prepared by microwave-assisted reduction of graphene oxide, and their electrochemical properties were compared with those of Ketjen Black and carbon nanotubes. The catalytic effect of the prepared graphene flake-air cathode was demonstrated using cyclic voltammetry and discharge–charge testing performed under a limited discharge capacity. The catalytic effect of graphene flakes was also supported by morphological and spectroscopic analysis of the discharge–charge products formed on the graphene surface. Scanning electron microscopy, X-ray diffraction, and Fourier-transform infrared spectroscopy revealed that Li₂O₂, Li₂O, and Li₂CO₃ were the main discharge products on all carbon-air cathode surfaces. Raman spectroscopy revealed that LiRCO₃ was additionally formed on Ketjen Black and carbon nanotubes during the first discharge; however, its formation was not observed on the graphene flakes. The catalytic effect of the graphene flakes and the absence of LiRCO₃ in the discharge product could explain the higher Coulombic efficiency in the discharge–charge tests.

1. Introduction

Rechargeable Li–O₂ batteries are emerging as a breakthrough technology for use as next-generation energy storage systems for electrical vehicles (EVs) owing to their high specific capacity. 1–3 During the discharge of a Li–O₂ battery, O₂ is reduced to form a solid discharge product such as Li₂O or Li₂O₂ on the surface of the carbon-air cathode. This material eventually covers the reaction sites and clogs the pores of the carbon structure within the air cathode. Different forms of carbon such as Vulcan XC-72, Ketjen Black (KB), and Super P have been investigated as air cathode materials. The discharge capacity of a Li–O₂ battery depends on its physical properties such as specific surface area and porosity of the carbon material in the air cathode, 4–9 and is in the range of around 2000–3000 mA h g⁻¹. 10–12 In the subsequent charging process, the discharge products are electrochemically decomposed to Li⁺ ions and O₂; 13 however, they are reported to be only partially decomposed, mainly due to the low electronic conductivity (≈10⁻⁴ S m⁻¹) of the solid products 14,15 and a weak catalytic effect of carbon toward oxygen evolution reactions (OER). 11

In order to improve the Coulombic efficiency and overpotential of the carbon-air cathode during charging, carbon nanocomposites with various metal and metal-oxide catalysts such as ñ-MnO₂, 6,16 MnCo₂O₄, 17 and Pt–Au nanoparticles 11,18 have been investigated. For example, a mesoporous NiCo₄O₉ nanoflake catalyst was reported to lower discharge–charge overpotentials and provide enhanced cycling stability compared to that of a pure carbon material (Super P) in 1 M Li bis(trifluoromethylsulfonyl)imide (LiTFSI) in tetraethylene glycol dimethyl ether (TEGDME) solution. 19 Graphene flakes (GF) consist of a few layers of graphene in which the carbon atoms are tightly packed into 2-dimensional (2D) honeycomb sp² carbon lattices that possess structural defects as well as a high concentration of edge sites. 20–22 Graphene has recently been investigated for use as an air-cathode material in Li–O₂ batteries. 23–26 Sun et al. investigated GF as an air-cathode material for non-aqueous Li–O₂ batteries for the first time, and reported a discharge capacity as high as 8705 mA h g⁻¹. 27 Zhang et al. reported a discharge capacity of 15 000 mA h g⁻¹ in an ether-based electrolyte from an air cathode composed of hierarchically porous graphene balls. This large discharge capacity was attributed to defects and functional groups within the graphene structure, which favoured...
the formation of isolated nanosized Li$_2$O$_2$ particles, and helped prevent air blocking in the air electrode. Yoo and Zhou evaluated GF for use as an air-cathode material in Li–O$_2$ batteries with an aqueous–non-aqueous hybrid electrolyte, demonstrating the electrocatalytic activity of GF toward the oxygen reduction reaction (ORR) in (1 M LiNO$_3$ + 0.5 M LiOH) aqueous solution. Wang et al. also reported the catalytic effect of GF, observing a smaller difference between the charge and discharge potentials of GF (1.22 V) compared to a Vulcan XC-72 carbon electrode (1.69 V) in a carbonate-based electrolyte.

In this study, we prepared GF via solid-state microwave irradiation treatment of graphite oxide (GO) under an Ar atmosphere and investigated its catalytic effect toward ORR and OER in a non-aqueous dimethyl ether (DME) electrolyte solution using cyclic voltammetry (CV) and discharge–charge tests. The discharge capacity for the discharge–charge tests was intentionally limited to 1280 mA h g$^{-1}$ within the potential window from 2.5 to 4.2 V (vs. Li/Li$^+$), as excess accumulation of the insulative discharge products might obscure the catalytic effect of GF due to the limited transport of Li$^+$ ions, O$_2$, and electrons in the discharge products. In addition to the electrochemical characterization of GF, morphological and spectroscopic analysis of the discharge–charge products on GF were performed to further investigate their formation and removal during discharge–charge cycles.

2. Experimental

2.1 Preparation of carbon-air cathodes

GO was synthesized from purified graphite powder using a modified Hummers method. GF was then synthesized from the as-prepared GO using a method reported in a previous study. The GF-air cathode was prepared as follows: GF was mixed with a polyvinylidene fluoride (PVDF, $M_w = 534,000$ g mol$^{-1}$, Sigma-Aldrich) binder at a weight ratio of 85:15 in N-methyl-2-pyrrolidone (NMP, Sigma-Aldrich, anhydrous, 99.5%), forming a slurry without using any additional conductive agent. The slurry was subsequently cast onto Teflon-coated carbon paper (TGP-H-060 Carbon Paper, Toray) to act as a gas-diffusion layer, with a carbon-loading density of 2.0 mg carbon cm$^{-2}$. The slurry-coated carbon-paper air cathodes were then dried at 100 °C in an oven for 24 h.

2.2 Electrochemical measurements

For electrochemical characterization of the GF-air cathode material, coin cells (2032-type, Welcos) were assembled in a glove box filled with purified Ar (99.999%). The coin cells were assembled in the following order: stainless-steel casing bottom, gasket, stainless-steel spring, stainless-steel disk spacer (0.5 mm thickness), Li-metal anode (16 mm diameter), separator (18 mm diameter), air cathode (14 mm diameter), stainless-steel cap with a hole. The cap of the coin cells had one hole with a diameter of 1 mm. The electrolyte was 1 M Li bis(trifluoromethanesulfonyl)imide (LiTFSI, Sigma-Aldrich, 99.95%) in dimethyl ether (DME, Sigma-Aldrich, ≥99%). A glass-microfiber filter paper (Whatman GF/D, 2.7 μm pore size) was used as the separator, and Li foil (Iljin Materials, 0.14 mm thickness) was used as the counter electrode. Finally, the assembled Li–O$_2$ coin cell was removed from the Ar-filled glove box and placed in a separate glove box filled with O$_2$ (99.995%) at a pressure of 1 atm, where all of the subsequent tests were carried out. For comparison purposes, air electrodes using KB (Ishin Chemtech) and carbon nanotube (CNT, Hanwha Chemical) materials were prepared and assembled in the same manner. The assembled coin cells were fixed into a 2032 coin cell holder (HITECH) in an O$_2$-filled glove box for electrochemical measurements. CV tests were performed with the coin cell using a Biologic potentiostat/galvanostat Model VMP2 (BioLab, Inc.) within a potential window of 2.0–4.5 V (vs. Li/Li$^+$) at a potential scan rate of 0.1 mV s$^{-1}$ at room temperature. Discharge and charge tests were performed at a constant current density of 0.4 mA cm$^{-2}$ (330 mA g$^{-1}$) from 2.5 V to 4.2 V to avoid electrolyte decomposition, while the discharge capacity of the air cathode was set to 1280 mA h g$^{-1}$ for investigation of the catalytic effects of GF, KB, and CNT on air-cathode performance.

2.3 Characterization of carbon materials and discharge products

The physical properties of GF were characterized using a variety of analytical techniques. Scanning electron microscopy (SEM, S-4300SE, Hitachi) was used to analyse structural and microscopic features of the carbon materials. X-ray diffraction (XRD, D8-Advance, Bruker) patterns were obtained on a diffractometer using a voltage of 40 kV and a current of 200 mA at a scan rate of 2° min$^{-1}$; the degree of graphitization of the carbon materials was subsequently calculated from the value of the (002) reflection.

Raman spectroscopy was carried out using a Raman microscope system (LabRam HR, Horiba Jobin Yvon) equipped with an Ar ion laser of wavelength 488 nm with 0.5 mW of laser power on samples, a 60 s exposure, and 600 gr per mm gratings. Peak intensities of the D and G bands (1360 cm$^{-1}$) were acquired at various points on the carbon powders, and then the average relative intensity ($I_D/I_G$) was calculated. N$_2$ adsorption–desorption isotherms of the carbon materials were measured using a fully automatic physisorption analyzer (ASAP 2020, Micrometrics Co.). The Brunauer–Emmett–Teller (BET) specific surface area was calculated from the adsorption data in the relative pressure ($P/P_0$) range of 0.05–0.2; total pore volume was determined from the amount of N$_2$ adsorbed at $P/P_0 = 0.98$. Pore-size distribution was calculated based on the desorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) method.

To characterize the discharge products, the discharged Li–O$_2$ coin cells were disassembled in the Ar-filled glove box, and the air cathodes were washed repeatedly with fresh anhydrous dimethyl carbonate. After washing, the cathodes were dried overnight under vacuum at room temperature. Discharge–product morphology was observed using SEM; care was taken to protect the samples from exposure to air during transfer to the SEM chamber, with a paraffin tape-sealed box prepared in the glove box used for the transport process. XRD analysis was performed on the discharged–charged carbon-air cathodes in an Ar-filled airtight holder with a 2θ range of 30–60° at a scan rate of 2° min$^{-1}$.
This range was chosen, as the main XRD peaks from the discharge products were known to occur within this range, with those from the carbon paper and electrolyte appearing outside of the range. Fourier-transform infrared (FTIR, Vertex 70, Bruker) spectra of samples were obtained by forming KBr pellets with the discharged–charged carbon materials from the air cathodes and taking measurements in the frequency range of 400–4000 cm\(^{-1}\) under an Ar atmosphere. Raman spectra of the electrodes were measured using a Raman microscope system (LabRam HR, Horiba Jobin Yvon) in the range of 100–2000 cm\(^{-1}\), with an Ar ion laser of wavelength 488 nm.

### 3. Results and discussion

#### 3.1 Physical properties of GF, KB, and CNT materials

Fig. 1 shows SEM images of the three different carbon materials used for preparing the air cathode. In this study, GF was prepared using a solid-state microwave-irradiation technique under an Ar atmosphere. As shown in the inset of Fig. 1(a), the GF exhibited a wrinkled or worm-like morphology, which is characteristic of the thermally exfoliated reduced GO.\(^{33-35}\) The graphene sheet edges were linked as a continuous sheet network, leading to the formation of a highly porous GF structure. As shown in Fig. 1(b), KB was composed of spherical carbon particles approximately 20–50 nm in diameter, and displayed a rough surface. The CNT material, as shown in Fig. 1(c), was observed to have an outer diameter ranging from 5 to 10 nm and a length of hundreds of nanometers within an entangled network.

Fig. 2 shows the physical properties of the three carbon materials, as analyzed using XRD, Raman spectroscopy, and \(\text{N}_2\) gas adsorption–desorption measurements. The degrees of graphitization were calculated using Bragg’s law from the value of the (002) reflection in the XRD spectra (Table 1). GF gave the highest \(d_{002}\) value of 3.78 Å, with a broad XRD peak visible around \(2\theta = 23^\circ\) (Fig. 2(a)), indicating that the graphene sheets in GF were relatively well exfoliated.\(^{36}\) KB was considered to be less graphitized than the CNTs, as it provided a higher \(d_{002}\) value of 3.68 Å.\(^{37,38}\) The CNTs were found to be the most graphitized carbon material among those investigated in this study, with a \(d_{002}\) value of 3.41 Å, which is quite similar to the theoretical value for graphite (3.35 Å).\(^{39}\)

Fig. 2(b) shows atomic bonding characteristics of the carbon materials, as analyzed by Raman spectroscopy. The spectra contained two prominent peaks at 1360 cm\(^{-1}\) and 1580 cm\(^{-1}\), corresponding to the D and G bands, respectively.\(^{40}\) The G band represents the first-order scattering of the \(E_{2g}\) mode from the \(sp^2\) carbon domains, and the D band originates from the disorder-induced mode associated with structural defects and imperfections.\(^{41}\) The intensity ratio \((I_D/I_G)\) is generally used as a measure to evaluate the quality of graphitic structures.\(^{40,42}\) The value for GF was calculated to be 0.82, while KB and CNTs gave higher values of 1.23 and 1.07, respectively, suggesting that GF had fewer defects than the other carbon materials.

Fig. 2(c) shows a linear \(\text{N}_2\) gas adsorption–desorption isotherm and the BJH pore-size distribution (inset) of the GF, KB, and CNT materials. The isotherm for the GF was noted to have a typical type IV shape. The steep increment in the adsorption capacity of GF at relative pressures \((P/P_0)\) ranging from 0.45 to 0.55 can be attributed to capillary condensation, with the corresponding hysteresis loop being characteristic of porous materials with a narrow mesopore size distribution.\(^{43}\) The isotherm for KB showed steep increments in the adsorption capacity at relative pressures \((P/P_0)\) around 0.5, with a clear hysteresis loop, indicating that KB also contains mesopores. On the other hand, the isotherm for the CNT material exhibited a gradual increase, with an adsorption step at a \(P/P_0\) value of 0.9, indicating that the CNT air cathode is less porous than the other carbon structures. The inset in Fig. 2(c) shows the pore-size distribution of the carbon materials obtained using the BJH method. The GF exhibited mesopores of around 3.5 nm in diameter, while the majority of pores in the KB were around 2 and 4 nm. In contrast, the pores of the CNT material were much larger, approximately 30–40 nm. The specific surface area and pore volume of the three materials are shown in Table 1.

#### 3.2 Electrochemical properties of GF, KB, and CNT-air cathodes

CV has been previously used to investigate the electrochemical properties of carbon materials as electrodes in air cathodes.\(^{16,44-46}\) In the present study, CV experiments were performed to evaluate the electrochemical properties of GF, KB, and CNT materials with respect to the ORR and OER in a potential window of 2.0–4.5 V (vs. \(\text{Li/Li}^+\)) at a scan rate of 0.1 mV s\(^{-1}\). Fig. 3(a) shows a comparison...
of the first-cycle voltammograms for GF, KB, and CNT-air cathodes under Ar (inset) and O₂ atmospheres. As shown in the inset of Fig. 3(a), all carbon-air cathodes examined showed a weak and monotonous current response at all potentials under an Ar atmosphere, which was attributed to the adsorption–desorption of Li⁺ on the carbon surface.⁴⁷,⁴⁸ The double-layer charging and discharging current increased in the order CNT < GF < KB, which is expected, as the current response due to the electric double-layer is proportional to the specific surface area of carbon used to prepare the electrode. The high voltage tail extending to 4.3 V during charging indicates decomposition of the DME electrolyte at potentials above this value.

On the other hand, under an O₂ atmosphere, each carbon-air cathode gave CVs with cathodic and anodic current peaks (Fig. 3(a)). Similarly-shaped CV peaks have been previously reported for a glassy carbon-air electrode in the DME electrolyte in a bulk electrolysis cell.⁴⁴ The cathodic current peak present in the CVs corresponds to the ORR (2Li⁺ + 2e⁻ + O₂ → Li₂O₂), which is responsible for the discharge of the air cathode, and the anodic current peak corresponds to the OER (Li₂O₂ → 2Li⁺ + 2e⁻ + O₂), which is responsible for the charge process. The theoretical potential for the ORR and OER is $E^\theta = 2.96$ V (vs. Li/Li⁺); however, the ORR potential was usually observed at around 2.7 V during discharge, with the OER being seen at around 4.3 V during charge.

The GF-air cathode gave ORR and OER peak current densities of around 3 A g⁻¹ carbon at 2.4 V and 1 A g⁻¹ carbon at 3.1 V, respectively. The KB-air cathode gave the highest ORR peak current among the three carbon-air cathodes, with a value of 5.3 A g⁻¹ carbon at 2.3 V (Fig. 3(a)), and also exhibited an OER current density of 0.8 A g⁻¹ carbon at 3.3 V. The CNT-air cathode gave ORR and OER current densities of 2.5 A g⁻¹ carbon at 2.15 V and 0.4 A g⁻¹ carbon at 3.45 V, respectively, with a broad current peak. It should be noted that the GF-air cathode exhibited the least cathodic and anodic overpotentials for ORR and OER among the three carbon-air cathodes under an O₂ atmosphere, corresponding to the smallest peak potential separation of 0.7 V in comparison to KB (1.0 V) and the CNT material (1.3 V).

The differences between the cathode materials discussed above are due to their different physical properties, and hence the catalytic effect of the carbon-air cathodes on ORR and OER kinetics.²⁷ The cathodic peak current density responsible for the ORR increased in the order CNT < GF < KB, which corresponded to the trend in the specific surface area of the three carbon materials. In general, having a large surface area and highly porous structure for the carbon component of these cathodes enhances ORR kinetics by providing easy access of electrolytic O₂ and Li⁺ to the air cathode surface.⁴⁴,⁴⁹ Moreover, the catalytic effect of the carbon material can lead to higher anodic peak current with less anodic overpotential for the OER in CV.²⁹ Despite the fact that GF had a smaller surface area than KB, the GF-air cathode showed a higher anodic current density for the OER than the KB cathodes, suggesting that the GF-air cathode is electrochemically more active toward the OER reaction than the KB cathode. Furthermore, the low anodic overpotential of the GF-air cathode supports the existence of a catalytic effect on the electrochemical discharge-product decomposition attributed to the carbon material.

Fig. 3 also shows the variation in the CV for the three different carbon-air cathodes under an O₂ atmosphere over 20 cycles. For all of the cathodes, the ORR and OER current
responses decreased during the repetitive CV cycling within the potential window of 2–4.5 V. For the GF-air cathode (Fig. 3(b)), the OER peak current centred at 3.1 V gradually decreased with cycling, disappearing around the 17th cycle. The ORR peak current at 2.4 V also gradually decreased; however, it was still visible during the 20th cycle, with a slight shift in the ORR potential from 2.4 V to 2.25 V. KB showed a decrease in the OER current density at 3.3 V upon cycling, with the OER current disappearing at the 9th cycle (Fig. 3(c)). Furthermore, compared to GF, the KB cathode showed a rapid decay in the ORR current density, with an ORR peak potential shift from 2.3 V to 2.17 V during cycling. For the CNT-air cathode, the anodic peak current at 3.45 V was barely seen after the third cycle, with a decrease in the cathodic peak current and shift in the peak potential also evident (Fig. 3(d)).

Since CV analysis suggested that GF was electrochemically more active towards the OER in comparison to KB and CNT, the discharge–charge behaviour was evaluated with respect to the discharge–charge profile and Coulombic efficiency. Fig. 4 shows the obtained discharge–charge profiles of the three carbon-air cathodes over 10 cycles at 0.4 mA cm$^{-2}$ (330 mA g$_{\text{carbon}}^{-1}$). In this study, the discharge capacity was limited to 1280 mA h g$^{-1}$ within the potential window from 2.5 to 4.2 V, as excess accumulation of the insulative discharge products might obscure the catalytic effect of GF due to the limited transport of Li$^+$ ions, O$_2$, and electrons in the discharge products. In addition, the discharge–charge potential range was set between 2.5–4.2 V to avoid decomposition of the electrolyte above 4.3 V, and the formation of irreversible by-products below 2.3 V.$^{16,45}$

Fig. 4(a) shows the discharge–charge profiles of the GF-air cathode for the first 10 cycles. The GF-air cathode showed a discharge onset potential of 2.8 V for the ORR, which is close to the thermodynamic equilibrium potential of 2.96 V (V vs. Li/Li$^+$). It should be noted that discharge proceeded at a constant potential plateau of 2.75 V for the 10 consecutive cycles. In contrast, during the charge cycle, sloping charge curves were observed, with an onset potential of 3.0 V; the onset potentials of ORR (2.8 V) and OER (3.0 V) from the galvanostatic test are in good agreement with those observed in the CV results shown in Fig. 3(b). More importantly, the shapes of the discharge–charge
profiles were well retained over the 10 cycles, and the initial discharge capacity of 1280 mA h g\textsubscript{carbon}\textsuperscript{−1} could be achieved in each discharge. Coulombic efficiency was calculated to be 99% for the first cycle and 87% for the 10th cycle for the GF-air cathode.

The discharge-charge profiles of the KB-air cathode in Fig. 4(b) showed an onset potential of approximately 2.7 V at the first discharge, decreasing gradually to 2.55 V upon cycling. The discharge potential plateau at the first discharge changed to a sloping discharge curve with repetitive cycling. Initially, a discharge capacity of 1280 mA h g\textsubscript{carbon}\textsuperscript{−1} was observed, however, this gradually decreased, reaching 92 mA h g\textsubscript{carbon}\textsuperscript{−1} at the 10th discharge. During charging of the KB-air cathode, sloping charge curves were observed with an onset potential of 3.1 V. A charge capacity of 874 mA h g\textsubscript{carbon}\textsuperscript{−1} was observed; however, this sharply decreased, reaching 81 mA h g\textsubscript{carbon}\textsuperscript{−1} at the 10th discharge.

Fig. 4(c) displays discharge-charge profiles for the CNT-air cathode over 10 cycles. The discharge onset potential for the ORR was noted at around 2.65 V, which decreased rapidly to 2.55 V upon cycling. The potential plateau at the first discharge changed to a sloping discharge curve after the third cycle. The first discharge capacity of 1280 mA h g\textsubscript{carbon}\textsuperscript{−1} rapidly decreased, reaching 180 mA h g\textsubscript{carbon}\textsuperscript{−1} at the 10th discharge. During the initial charging of the CNT-air cathode, steep sloping charge curves were observed, with an onset potential of around 3.15 V. The deep discharge-charge profiles of the GF, KB and CNT-air cathodes in the potential range of 2.5–4.2 V (vs. Li/Li\textsuperscript{+}) also showed the highest Coulombic efficiency for GF (see ESI,† Fig. S1). Analysis of the CV and discharge-charge profiles clearly shows that GF is the more electrochemically active of the three carbon-air cathodes (including KB, CNT) toward ORR and OER.

The significant differences observed in the electrochemical properties of the three carbon-air cathodes employed in Li–O\textsubscript{2} batteries using DME electrolyte can be ascribed to the differences in their physical properties and catalytic activities. GF, produced from the reduction of GO, contains a mixture of \textit{sp\textsuperscript{2}} and \textit{sp\textsuperscript{3}}-hybridized carbon atoms, along with defects and oxygen functionalities such as carboxyl, carbonyl, hydroxyl, epoxy, and peroxy groups, with carboxylic acids the most likely to be located along the sheet edges.\textsuperscript{50,51} Zhang et al. suggested that the defects in the GF structure might facilitate the ORR and hinder the migration of Li\textsubscript{2}O\textsubscript{2} on the carbon surface during the OER.\textsuperscript{6} In addition, it was previously reported that the edge sites of graphene sheets could have specific chemical reactivities compared with non-edge carbon atoms because the carbon atoms at the edge of graphene sheets have partial radical character.\textsuperscript{29,52} Therefore, the enhanced catalytic effect of GF on the ORR and OER might come from the relatively large number of edge sites introduced into the GF during its synthesis. The detailed mechanisms of ORR and OER on GF are not yet completely clear and are currently under investigation.

The morphological features of the air electrodes during discharge-charge were examined using \textit{ex situ} SEM at different states of the cycling process. Fig. 5 shows SEM images of the GF-air cathode after the first discharge (a), the first charge (b), and the 10th charge (c) at 0.4 mA cm\textsuperscript{−2} (330 mA g\textsubscript{carbon}\textsuperscript{−1}) with a controlled discharge capacity of 1280 mA h g\textsubscript{carbon}\textsuperscript{−1}. After the first discharge, the GF surface was seen to be covered with particles of discharge material several nanometers in size, while the macroporous structure was retained. After the first charge, most of the discharge products disappeared from the GF surface, mainly due to their electrochemical decomposition.
during charging. After the 10th charge, the GF surface appeared partially covered with the discharge products; however, the macroporous nature of the GF in the air cathode was retained (Fig. 5(c)).

Fig. 5 also shows SEM images of the KB-air cathode. After the first discharge (Fig. 5(d)), discharge products covered the KB-air cathode, while the morphology of the as-prepared electrode was retained. After the first charge (Fig. 5(e)) however, the solid product formed during the first discharge process covering the KB surface was still evident. After the 10th charge (Fig. 5(f)), the KB-air cathode appeared heavily covered, with the pores between the carbon nanoparticles filled with solid products; further, the initial structural features of the KB air cathode were no longer evident. The SEM image of the CNT-air cathode after the first discharge (Fig. 5(g)) showed disk-shaped discharge products covering the surface, with the morphology of the as-prepared CNT material not visible. After the first charge (Fig. 5(h)), the discharge products appeared to be removed, with the initial morphology of the as-prepared CNT electrode being retained. After the 10th charge (Fig. 5(i)), the CNT material appeared covered with solid products, with the macroporous nature lost.

Analysis of SEM images of the GF, KB, and CNT materials acquired at different states of the cycling process indicates that the GF was able to electrochemically decompose the discharge product in the subsequent charge cycle, retaining the initial macroporous nature of the carbon-air electrode, in contrast to the KB and CNT materials. The morphological features of the air electrodes during discharge–charge examined by ex situ SEM at different states of the cycling process are consistent with the CV analysis and discharge–charge profiles shown in Fig. 3 and 4, respectively.

3.3 Discharge product analysis

The discharge products found on the different carbon-air cathodes at different cycles of the discharge–charge processes were characterized using XRD, FT-IR, and Raman spectroscopy. Fig. 6 shows the XRD patterns of the GF-air cathode with...
discharge capacity controlled at 1280 mA h g$_\text{carbon}$$^{-1}$. The intense peak at around $2\theta = 54^\circ$ was attributed to the carbon paper. The XRD analysis indicated that Li$_2$CO$_3$ was formed during the first discharge in the DME electrolyte, and was not removed in the subsequent charge cycle for all carbon materials tested in this study. Formation of Li$_2$CO$_3$ was also confirmed from the presence of peaks at 1640 cm$^{-1}$, 1360 cm$^{-1}$ ($\text{–LiCO}_3$), 1436 cm$^{-1}$ (O–CO$_2$), and 867 cm$^{-1}$ (C–O–C). For Li$_2$CO$_3$, the peak intensities increased gradually upon repeated discharging, and decreased slightly upon subsequent charging, indicating that Li$_2$CO$_3$ was hardly decomposed during charging. Analysis of the FT-IR spectra of KB and CNT-air cathodes indicated the formation of the same products after the first discharge. However, a decrease in LiO$_2$ and Li$_2$O$_2$ peak intensities of around 505 cm$^{-1}$ and 564 cm$^{-1}$ (Li–O) after the first charge was clearly less than that for GF, suggesting that discharge product removal was more effective for GF (see ESI† Fig. S2).

Fig. 8 shows the Raman spectra of GF, KB, and CNT-air cathodes. The $I_D/I_G$ ratio of the three carbon materials showed little change, regardless of the discharge–charge state. It should be noted that new peaks appeared during discharge at 1130 cm$^{-1}$ and 1525 cm$^{-1}$ for the KB and CNT-air cathodes, respectively, corresponding to alkyl C–C stretching modes. These Raman peaks did not disappear during the subsequent charge. Luntz et al. reported the formation of alkyl groups of LiRCO$_3$ on a glassy carbon-air cathode in the DME electrolyte. LiRCO$_3$ was found to be an irreversible by-product of the electrochemical reaction between Li$_2$O$_2$ and DME during discharge–charge. LiRCO$_3$ has been previously reported as being one of the remaining solid products covering the air cathode reaction sites, increasing
the overpotential for the ORR and OER upon cycling.\textsuperscript{45,60} In contrast, in the present study, the GF-air cathode did not show any Raman peaks due to LiRO\textsubscript{3} during repeated discharge. This might explain the markedly different discharge–charge behaviours of GF in comparison to the KB and CNT-air cathodes shown in Fig. 4. The possible formation of LiRO\textsubscript{3} on KB and CNT-air cathodes is currently under investigation.

4. Conclusions

In this study, we employed GF as an air-cathode material for Li–O\textsubscript{2} batteries, and investigated its electrochemical properties in the DME electrolyte. GF was prepared by microwave-assisted reduction of GO, and its electrochemical properties were compared with those of KB and CNT-based air cathodes. The GF-air cathode showed peak-shaped CVs under an O\textsubscript{2} atmosphere, with lower ORR and OER overpotentials observed in comparison to KB and CNT. The catalytic effect of the GF-air cathode was confirmed using discharge–charge testing, and was corroborated by morphological and spectroscopic analyses of discharge–charge products on the surface of the GF. Raman spectroscopy revealed that LiRO\textsubscript{3} was formed on the KB and CNT during the first discharge, but not on the GF. In combination with the catalytic effect of GF, this might explain the higher Coulombic efficiency of GF observed in the discharge–charge tests. These results demonstrate that GF has great potential for use as a cathode material for improved Li–O\textsubscript{2} batteries.

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