A composite made from hollow polyhedron copper oxide and graphene oxide was synthesized by sintering a Cu-based metal–organic framework (Cu-MOF) embedded with exfoliated graphene oxide. As a proof-of-concept application, the obtained Cuox–rGO materials were used in a lithium-ion battery and a sodium-ion battery as anode materials. Overall, the Cuox–rGO composite delivers excellent electrochemical properties with stable cycling when compared to pure CuO–rGO and Cu-MOF.

The energy issue is one of the very hot topics in the society due to the development of the economy, which requires cost-effective, efficient and environmentally benign energy storage devices that can empower energy demanding areas. Owing to their high energy density, light weight and long cycle lives, rechargeable batteries (RBs) have shown considerable promise for storage applications.1–5

Metal–organic frameworks (MOFs) are a novel class of porous materials, which have attracted considerable interest due to their potential applications in catalysis, nonlinear optics, ion exchange, gas storage and separation.6–10 Among the various forms of carbonaceous materials, graphene and graphene-based materials are on the top notch, owing to the specific and very unique structural, mechanical, and electronic properties of these one-atom-thick sheets.11,12 Graphite oxide (GO) is formed by treating graphite with very strong oxidizing agents.13 Oxidation of graphite results in the introduction of epoxy and hydroxyl groups into the graphene layers and carboxylic acid groups mainly located at the edges of the layers.14,15

Recently, the hybrids of MOFs and graphene derivatives have attracted significant attention because of their good structural scaffolds as they stabilize the physical structure during charge-induced volume expansion, which further improved the conductivity of metal oxides. Graphene has a wide scope to act as an ideal conducting additive for hybrid composite electrodes.16–26 Furthermore, when GO was reduced to reduced graphene oxide (rGO), it can overcome the poor electrical conductivity of the MOF; thus MOF/rGO composites can be used as promising electrode materials for electrocatalysis.27 To date, there have been only a few reports on GO–CuO composites prepared by chemical methods.28–33 Herein, we report a simple synthetic strategy to prepare Cuox–rGO (CuO/Cu2O hollow polyhedrons on rGO). Furthermore, applications, such as lithium-ion batteries (LIBs) and sodium-ion batteries (NIBs), were demonstrated.

The morphology of the Cu-MOF and Cuox–rGO is shown in the ESI† (Fig. S4–S9). Cyclic voltammetry (CV) was employed to study the reaction mechanism during electrochemical cycling in half-cell assembly (Li/Cuox–rGO) between 0.005 and 3 V vs. Li at a slow scan rate of 0.1 mV s–1 (see Fig. 1A). During the first cathodic scan, a prominent peak at ~1.08 V is noted, which is attributed to the formation of the Cu2O phases and associated structural destruction as well. Another small cathodic peak at ~0.69 V corresponds to the further reduction of CuO to metallic Cu0 in the Li2O matrix, though decomposition of the electrolyte solution cannot be ruled out. Decomposition of the electrolyte solution leads to the formation of polymeric layers and inorganic byproducts in the form of a solid electrolyte interface (SEI). During the anodic scan, the peak at ~2.45 V corresponds to the oxidation of Cu0 to CuO as well.34–37 From the 2nd cycle onwards, cathodic peak potentials were slightly shifted towards higher voltages, whereas no significant shift in the peak positions is noted during the anodic scan. Accordingly, the reduction of CuO to Cu2O occurs at ~1.3 V and formation of metallic Cu0 takes place at ~0.84 V with huge suppression of area underneath the curve when compared to the first cathodic sweep.15 However, there is no deviation observed during successive cycles except overlapping of the traces which implies good cyclability of the CuO nanostructures during cycling. The formation of an intermediate phase (Cu2O) has been convincingly proven.

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A constant current density of 200 mA g\(^{-1}\) was used to electrochemically exfoliate graphene. This leads to well-dispersed graphene and an increase in the active surface area, which is beneficial for the large area of anode materials. Organic conductive polymers, and electrolyte decomposition, result in loss mainly from the diverse irreversible processes, such as the formation of metal-oxide electrodes. This results in a slow increase in the specific capacity during cycling, as observed in the case of Cu\(_{ox}\)-rGO, with a capacity increase of about 1490 mA h g\(^{-1}\). The capacity of Cu\(_{ox}\)-rGO electrodes is consistent with the large area of anode materials and the unique structural advantage of Cu\(_{ox}\)-rGO, which is expected to contribute to the electrochemical exfoliation of graphene sheets.

**Fig. 1.** Lithium-ion-battery performance: (A) cyclic voltammograms of the Cu\(_{ox}\)-rGO composite electrode at a scan rate of 0.1 mV s\(^{-1}\) between 0 and 3.0 V, (B) discharge–charge curves of the Cu\(_{ox}\)-rGO composite electrode between 0.05 and 3.0 V at 200 mA g\(^{-1}\) current rate, (C) cycle performance of various electrodes at 200 mA g\(^{-1}\) current rate, and (D) cycle performance of the Cu\(_{ox}\)-rGO composite electrode at different current rates.

Galvanostatic charge–discharge studies were conducted for Cu\(_{ox}\)-rGO nanostructures in half-cell assembly (Li/Cu\(_{ox}\)-rGO) at a constant current density of 200 mA g\(^{-1}\) and the data are provided in Fig. 1B. In the figure, there are two obvious sloping potential ranges (1.35–1.0 and 1.0–0.05 V vs. Li\(^+\)/Li, respectively) in the first discharge process, which are in accordance with the two cathodic peaks in the CVs in Fig. 1A. During the following discharge process, all the slopes become narrow and the plateau slightly upward. Upon the charging process, a plateau at about 2.45 V can be clearly identified during all the charge cycles was recorded. The half-cell delivered a capacity of \(\sim 1324\) and \(\sim 690\) mA h g\(^{-1}\) for first discharge and charge, respectively. This can be attributed to the large electrochemical active surface area of well-dispersed graphene and significant surface areas of SEI in the well-dispersed Cu\(_{ox}\). As expected, a high irreversible capacity of 52.1% is noted in the first cycle, the initial capacity loss mainly results from the diverse irreversible processes, such as the formation of SEI layer, organic conductive polymers, and electrolyte decomposition, which are common for most anode materials.

**Fig. 1C.** Shows the cycling performance of different electrodes (GO, MOF, CuO–rGO blank and Cu\(_{ox}\)-rGO) at a current density of 200 mA g\(^{-1}\). It can be seen that, when compared with other samples, the electrode with Cu\(_{ox}\)-rGO exhibits the best electrochemical performance with a reversible capacity of about 1490 mA h g\(^{-1}\) after 220 cycles. It is remarkably noticed that the capacity decreases first and reaches a minimum (650 mA h g\(^{-1}\)) in the 3rd cycle. It rises gradually afterwards and reaches about 1490 mA h g\(^{-1}\) in the 220th cycle. It can be seen that the capacity of Cu\(_{ox}\)-rGO recovers after initial fading for the first few cycles. The slow increase in the specific capacity during cycling has also been reported for metal-oxide electrodes. In this case, the capacity increases by a significant amount to 1490 mA h g\(^{-1}\) in the 220th cycle. This increase in the capacity might be a result of electrochemical exfoliation of graphene sheets, which seems to be more at a higher current rate and capable of bringing extra Li into active traverse between electrodes. Exfoliation of graphene sheets is proven to create additional room (availability of an active surface area) for increased Li adsorption onto their surfaces. This kind of increase in the capacity due to volumetric changes caused by exfoliation of graphene sheets was observed in the case of carbon nanofibers upon long-term cycling, but in the case of Cu\(_{ox}\)-rGO, it is observed at a much early stage of aging. Here the surfaces of Cu\(_{ox}\) nanoparticles, which are expected to possess highly catalytic nature, are expected to avoid Li dendrite formation by decreasing the repulsive interactions between Li–Li ions like electron-deficient dopants in the case of modified graphene. Thus, Cu\(_{ox}\) nanoparticles also reasonably support the long-time sustainability of anode functioning without failure yet with increased capacity. Recent report of MgO-decorated few-layered graphene by Shaikshavali et al. supports this explanation. In the meantime, the Cu\(_{ox}\)-rGO electrode exhibits outstanding rate capability at different current densities of 200–4000 mA g\(^{-1}\) (Fig. 1D). The cell also shows good capacity retention even after changing back the current density of 200 mA g\(^{-1}\). Moreover, the prominent structural advantage of Cu\(_{ox}\)-rGO enables substantially improved cycle life at a high current rate (1000 mA g\(^{-1}\)). Cu\(_{ox}\)-rGO still exhibited \(~ 1100\) mA g\(^{-1}\) after 600 cycles (Fig. 3A). These results imply that the electrode structure of Cu\(_{ox}\)-rGO allows it to exhibit stable cycle performance at a high rate over 600 cycles without capacity fading. Overall, it is clear that the Cu\(_{ox}\)-rGO composite possesses excellent properties such as high rate capability, good cycling performance, and a capacity that increases upon cycling, which are very useful for high-power battery applications, such as in hybrid electric vehicles, power tools, and power backup systems.
two different time constants, which indicates that Cuox–rGO not only possesses low SEI resistance (≈114 ohm) but also very low charge transfer resistance (≈166 ohm) in comparison with the rest of the materials (Fig. 2A and Table S1, ESI†). This significant reduction in the charge transfer resistance stems from GO and Cuox, in which GO provides better electrode to electrolyte contact while Cuox provides a facile path for the conduction of the charge carriers. In the very low frequency region, a straight line in the case of Cuox–rGO renders information about the good capacitive behavior of the electrode material. The modeling of EIS spectra for MOF and Cuox–rGO electrodes' surface was done using the Randles electrical equivalent circuit (Fig. S10, ESI†). The results from the fit are presented in Table S1 (ESI†).

In order to investigate the change in the EIS spectra of the Cuox–rGO electrode, EIS spectra of the electrode before and after 1st cycle, 15th cycle, and 50th cycle, and so on were collected up to 300 cycles, and are presented in Fig. 2B. It is evident from the EIS analyses that the charge resistance of the electrode increases with the cycling, which is reflected by the disappearance of the peak in the low frequency region. When the resistance for the intercalation reaction tends to infinity, the only reaction which could presumably occurs at the electrode/electrolyte interface is the adsorption of the ions, which is evident from the straight line in the low frequency region after 300th cycles.

It is also interesting to note that the capacity of the Cuox–rGO electrode shows two major trends. For the first few cycles, the capacity shows a decreasing trend, while for the next cycles, the capacity trend increases. The initial decrease may be due to the extraction of Li from Li2O being thermodynamically impossible, which has formed during the transformation of Cu0 to Cu2+.47 Electrochemical impedance spectroscopy (EIS) analysis was performed in the samples' charge/discharge tests in order to obtain the charge-transfer resistance and investigate the kinetic behavior of the samples. The results revealed that the decrease in capacity upon cycling may be due to two factors, namely, low lithium-diffusion processes and large Li+ charge-transfer resistance (high polarization), which are also in good agreement with our study which states that the impedance of the cell before cycling is smaller than that of the cell after cycling (Fig. 2B).

On the other hand, the trend towards increasing capacity could be at least partly explained by the following reasons: (1) decreased cell resistance, (2) the effects of electrochemical milling, which can change the morphology of a material and reduce the particle size. The first reason may relate to the decrease in the cell resistance during the charge/discharge reaction, as shown in Fig. 2B. In the figure, the impedance of the cell before cycling is larger than that of the cell after the 15th cycle, and it becomes smaller after further charge-discharge up to 300 cycles, which is in good agreement with the capacity rise phenomena seen in CuO materials.48 This could be explained as follows: the initial production of Cu0 nano-grains from the reduction of Cu2+ by Li during cycling results in capacity fading, but after cycling over a long period, they may become active and participate in reactions that enhance the electrochemical reactivity. By offering high Li+ diffusion coefficients and a large amount of contact surface area between the electrode and electrolyte, copper can quickly absorb and store vast numbers of lithium ions without causing any deterioration in the electrode.49 The second reason may be due to the electrochemical milling effects, which change the morphology and decrease the size of the metal particles as well.48,50 The results reported are consistent with the second reason and are well supported by the SEM images of the electrode before and after 600 cycles at 1000 mA g⁻¹ current rate. (Fig. S11, ESI†). Such a structural change is well understood to improve and boost the reaction with lithium materials.

Fig. 3B shows that the electrochemical performance of Cuox–rGO was investigated using Na half cells in the range of 0.005–3.0 V. It displays typical charge–discharge curves of Cuox–rGO at a current density of 500 mA g⁻¹. In the first cycle, it deliver the discharge and charge capacities of 1060 and 439 mA h g⁻¹, respectively, showing a Coulombic efficiency of ≈41.41%. This is caused by the side reactions of the electrolyte and the formation of SEI. For the evaluation of the long-term cycle stability of the Cuox–rGO electrode, the electrode was galvanostatically discharged and charged at 500 mA g⁻¹ for...
3400 cycles (Fig. 3C). Practically no capacity decrease was observed. The superior cycle stability of the Cuox–rGO electrode for reversible Na+ storage was highly repeatable. Fig. 3D shows the rate capability of Cuox–rGO to be 100 to 4000 mA g−1. The test began with a current density of 100 mA g−1, where the discharge capacity was consistently ~290 mA h g−1 for the first ten cycles. When the current density was increased in steps to 200, 500, 1000, 1500, 2000, 3000 and 4000 mA g−1, the capacity decrease was very small for a battery material. The discharged capacities were retained when the current density was returned to 100 mA g−1. The negligible changes in discharge capacity with current density changes indicate the resilience of the Cuox–rGO hybrid structure. Evidently the large interlayer spacing allowed Na+ transport to be carried out at high rates (high current densities) without causing irreversible changes in the hybrid structure.

In summary, we successfully prepared a Cuox–rGO composite by the use of MOFs as precursors along with metal oxide and graphene oxide as backbones through a facile two-step annealing process. As a proof of concept, the obtained Cuox–rGO composite was used in lithium-ion and sodium-ion batteries.

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