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Comparing the physical properties summarized in Table 1 and in FIG. 2 with the micrographs in FIG. 1, it is most likely that the pore size, pore volume, and surface area data represents the average size of the open channels which are residing in the meso-pore range suitable for the formation of tri-phase regions. Since there appear to be fewer and smaller pores in the graphene-based air electrode (relative to as-received graphene), the improvement in performance is most likely explained by the formation of the network of channels through the random arrangement of graphene nanosheets, which define flow paths through the electrode. The natural folding areas and the inter-layer spaces between the graphene nanosheets as shown in FIG. 1 result in externally formed channels that can be utilized as flow paths and/or as storage places for discharge products.

FIG. 3 is a graph of the discharge curve for a Li-air battery using a graphene-based air electrode according to embodiments of the present invention. The cell was tested in pure oxygen (~2 atm) at a current density of 0.1 mA/cm². A very high capacity of greater than 8000 mAh/g is achieved when discharged to 2.6 V. A relatively flat plateau is observed at around 2.8 V similar with other air electrodes using different carbons.

The recharge-ability of the Li-air battery using a graphene-based air electrode is plotted in FIG. 4a. The data shown in FIG. 4a indicates that the graphene-based air electrode is rechargeable. Other carbon-based air electrodes with highly porous structures usually have a high surface area (2672 m²/g for Ketjenblack as an example) which can lead to significant decomposition of the organic electrolyte during the charge process. For comparison with FIG. 4a, the rechargeability of a common Li-air battery using Ketjenblack-based air electrode is plotted in FIG. 4b. After 5 cycles the voltage of the Ketjenblack-based Li-air cell shows unstable fluctuation related to electrolyte decomposition. In contrast, the embodiments of the graphene-based air electrodes described herein exhibit a relatively low surface area of 590.3 m²/g (Table 1). The limited surface area appears to result in reduced electrolyte decomposition on the surface of graphene nanosheets at voltages higher than 4.2 V. In some embodiments, a transition metal or transition metal catalyst deposited on the graphene nanosheets can further improve the cycling stability and to reduce the over potential during charge processes.

The tests described above were performed in a pure oxygen atmosphere. In order to evaluate the performance of the embodiments of the graphene-based air electrode in an ambient environment, a pouch-type cell was prepared as illustrated in FIG. 5a. The size of the air electrode was 2x2 cm² with a carbon loading of 4 mg/cm². FIG. 5b shows the discharge curve of the pouch-type Li-air battery using graphene-based air electrodes when operated in ambient conditions. A stable plateau is observed between 2.7-2.8 V and the discharge capacity was 5093 mAh/g carbon at 0.1 mA/cm² in the ambient environment.

Referring to FIG. 6, embodiments of the present invention utilizing electrolytes comprising glymes, ethers, or both can result in specific capacities exceeding approximately 15,000 mAh/g. The data provided in FIG. 6 was acquired on a Li-air cell having an electrode with randomly arranged graphene nanosheets, as described elsewhere herein, in conjunction with an electrolyte comprising lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) in tri(ethylene glycol) dimethyl ether (Triglyme). Alternative electrolytes can include those that comprise Triglyme, butyl glyme, tetra(ethylene glycol) dimethyl ether (i.e. Tetraglyme), di(ethylene glycol) dimethyl ether (i.e. Diglyme), and di(propylene glycol) dimethyl ether (i.e. diproglyme). Another particular example of an electro-

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lyte includes LiTFSI in dimethylene glycol dibutyl ether (or Butyl diglyme). Generally speaking, it is preferable to utilize an electrolyte that is stable and yields Li₂O₂ during the discharge process of Li-air batteries. X-Ray Diffraction (XRD) patterns (data not shown) indicate that both LiTFSI in Triglyme and LiTFSI in butyl diglyme can result in discharge products comprising Li₂O₂. Further still, the liquid electrolyte can comprise compounds such as Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI), lithium bis(oxalate)borate (LiBOB), LiPF₆, LiBF₄, LiAsF₆. Exemplary solvents in addition to those listed elsewhere herein, can include, but are not limited to, ethylene carbonate (EC), propylene carbonate (PC), dimethyl ether (DME) solvent, diethylene carbonate (DEC), ethyl methyl carbonate (EMC), and combinations thereof.

One of several available methods for making the graphene-based electrodes described elsewhere herein includes mixing dispersed graphene nanosheets with a binder and then forming them into electrodes. For example, as-received graphene can be dispersed in de-ionized water or other organic solvent and stirred. A PTFE emulsion (60% solids) can be added drop by drop into the graphene dispersion while stirring. The weight ratio of graphene to PTFE can be between 25:75 and 95:5. Preferably, the ratio is approximately 75:25.

The graphene and PTFE mixture can be stirred for an additional two hours and then dried in air at 80° C. overnight. The resultant powder mixture can be fed into a roller having a roller pressure between 10 and 120 psi. Preferably, the pressure is approximately 80 psi. The final loading in the rolled powder can be between 1 and 10 mg graphene/cm². Preferably, the loading is approximately 2 mg graphene/cm².

A conductive support, which can include, but is not limited to a nickel mesh or aluminum mesh can be embedded into the rolled graphene. The electrode can then be punched directly from rolled graphene into a desired shape and size.

In some embodiments, the graphene can be mixed with other mesoporous carbons such as Ketjenblack to improve the mesopore volume of the whole electrode. Preferably, the mesoporous carbons have a mesopore volume larger than 1 cc/cm³. The mixture of the randomly arranged graphene with the mesoporous carbon can provide both the network of channels as well as increased porosity for improved storage of reaction products. Exemplary reaction products in Li-air batteries can include Li₂O₂ and Li₂O. The ratio of graphene to other mesoporous carbons can vary from 100:0 to 5:95, preferably 50:50.

Furthermore, different catalysts such as Pt, Pd, Au, Cu, Ag, V₂O₅, Fe₃O₄, Cr₂O₃, MnO₂, Co₃O₄, NiO can be deposited on the graphene nanosheets homogeneously to promote oxidation reactions such as Li₂O₂ in Li-air batteries or ZnO in Zinc-air batteries. One method for catalyst deposition includes self-assembly.

While a number of embodiments of the present invention have been shown and described, it will be apparent to those skilled in the art that many changes and modifications may be made without departing from the invention in its broader aspects. The appended claims, therefore, are intended to cover all such changes and modifications as they fall within the true spirit and scope of the invention.

We claim:

1. A metal-air battery having a specific capacity greater than or equal to 5000 mAh/g graphene/carbon and having a metal electrode comprising Li and an air electrode comprising graphene, the air electrode comprising randomly arranged graphene nanosheets forming a network of channels defining continuous flow paths through the air electrode and by oxygen diffusing through the channels.