GRAPHENE-BASED BATTERY ELECTRODES HAVING CONTINUOUS FLOW PATHS

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

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BACKGROUND

Among all of the different electrochemical couples upon which energy storage devices can be based, metal-air systems can exhibit the largest theoretical specific energies. For example, a lithium-air system can exhibit a theoretical specific energy of 11,972 Wh/kg. However, electrochemical performance of metal-air batteries can depend greatly on many factors including the properties of the carbon-based air electrode. While various nanostructured carbon materials have been explored in attempts to improve metal-air energy storage devices, the practical capacity, specific energy and rate performance of such devices has not been sufficient for most energy storage applications. Accordingly, an improved metal-air energy storage device is needed.

SUMMARY

The present invention includes batteries having electrodes comprising graphene nanosheets and methods for forming such electrodes. In one embodiment, the air electrode of a metal-air battery is characterized by randomly arranged graphene nanosheets forming a network of channels defining continuous flow paths through the air electrode and by oxygen diffusing through the channels. Exemplary metals in the metal-air batteries can include, but are not limited to Zn, Na, Mg, Fe, Ca, or Al. Preferably, the metal comprises Li. The graphene nanosheets can on average be less than 1 μm in length, width, or both. In particular examples, the graphene nanosheets on average are less than 30 nm in length, width or both.

The air electrode can further comprise mesopores adjacent to the channels, wherein discharge product is stored in the mesopores. In some embodiments, the mesopore volume can be enhanced by mixing a highly mesoporous carbon material with the graphene nanosheets. Preferably, the carbon material itself has a mesopore volume greater than 1 cc/g. Storage of discharge products in the mesopores can minimize blockage of the channels to maintain flow paths for oxygen. Preferably, the channels can have an average diameter between 0.1 and 10 μm. In some instances, the graphene nanosheets can be modified to improve performance. For example, in one embodiment, the graphene nanosheets can be fluorinated and at least a portion of the electrode can comprise fluorinated graphene nanosheets (CF_x). In particular examples, x can be between 0.5 and 1.5. In another embodiment, a catalyst comprising a transition metal or a transition metal oxide can be deposited on surfaces of the electrode such as on the graphene nanosheets and/or on the mesopores.

Embodiments of the metal-air batteries described above and elsewhere herein can have a specific capacity greater than or equal to 5000 mAh/g active material (i.e., graphene/carbon).

In a particular embodiment of the present invention, a lithium-air battery has a specific capacity greater than or equal to 5000 mAh/g active material and has an air electrode comprising graphene. The air electrode comprises randomly arranged graphene nanosheets forming a network of channels defining continuous flow paths through the air electrode in which oxygen diffuses. The air electrode further comprises a carbon material mixed with the graphene nanosheets, wherein the carbon material has a mesopore volume greater than 1 cc/g. The air electrode can further comprise a transition metal or a transition metal oxide deposited as a catalyst on surfaces of the electrode, such as on the graphene nanosheets and/or on the mesopores. In preferred embodiments, the channels have an average diameter between 0.1 and 10 μm. Furthermore, at least a portion of the electrode can comprise fluorinated graphene nanosheets (CF_x).

While some aspects of the present invention are particularly applicable to metal-air batteries, the present invention is not necessarily limited to metal-air batteries. For example, some embodiments encompass metal batteries or metal-ion batteries. Other embodiments encompass batteries having a cathode comprising graphene and a liquid electrolyte. Similar to embodiments described elsewhere herein, the cathode is characterized by randomly arranged graphene nanosheets forming a network of channels. In the context of liquid electrolytes, the channels define continuous flow paths through the cathode for the liquid electrolyte. In one instance, the battery can have an anode comprising lithium. The anode can comprise lithium metal or lithium-based compounds. Exemplary lithium-based anodes can include, but are not limited to LiC_6, Li_xSi (x=0.5 to 4.4), Li_xSn (x=0.5 to 4.4), Li_xSnO_2, and Li_xTiO_y, and $Li_5Ti_4O_{12}$. In another example, the battery is an aqueous Li-air battery. In some embodiments, the graphene nanosheets can be less than 1 μm in length, width, or both. More particularly, the graphene nanosheets are less than 30 nm in length, width or both. In other embodiments, the graphene nanosheets are fluorinated and at least a portion of the electrode comprises fluorinated graphene (CF_x). In some instances, x can be between 0.5 and 1.5 and/or the batteries can be configured either as primary lithium batteries or as rechargeable lithium batteries.

In any of the embodiments utilizing liquid electrolytes, the electrolyte preferably comprises glymes, ethers, or both. Exemplary ethers and glymes include, but are not limited to, 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). Particular examples of electrolytes include Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) in tri(ethylene glycol) dimethyl ether (Triglyme) and LiTFSI in di(ethylene glycol) dibutyl ether (or Butyl diglyme). Most preferably, the electrolytes comprise solvents that form Li_2O_2 discharge products.

In a particular embodiment of the present invention, a lithium-based battery having a specific capacity greater than or equal to 8000 mAh/g graphene/carbon, comprises an electrode in which graphene nanosheets are randomly arranged to form a network of channels that define a continuous flow path for fluids through the electrode. A carbon material is mixed with the graphene nanosheets, wherein the carbon material has a mespore volume greater than 1 cc/g. An electrolyte in the battery comprises glymes, ethers, or both. While reaction products can often contain mixtures of compounds, in some preferred embodiments, a discharge product comprises Li_2O_2.

A method for forming the electrodes described herein can comprise the steps of dispersing graphene in water or other solvents and adding a binder to the dispersed graphene to form a mixture. The weight ratio of the graphene to the binder can range from 25:75 to 95:5. The mixture is then dried to