

Graphene-based Composites for Electrochemical Energy Storage

by James G. Radich, Paul J. McGinn, and Prashant V. Kamat

This article focuses on graphene-based electrodes for electrochemical energy conversion and storage devices.^{1,2} As elaborated in the other feature articles in this issue, graphene is a 2D “flat mat” consisting of a honeycomb-like structure of carbon atoms with sp^2 bonding character for each carbon. It exhibits excellent electrical conductivity and mechanical strength, and can be synthesized in a number of ways. Most syntheses involve first oxidizing graphite to graphene oxide (GO), a widely used method developed many years ago and referred to as Hummers Method.³ The graphitic carbon is dissolved in sulfuric acid along with other oxidants such as sodium nitrate during sonication, and $KMnO_4$ is slowly added to complete the oxidation process. Washing and rinsing allows for a fully exfoliated GO suspension in water, ethanol, and other polar solvents, that can be prepared as a stable colloid for months. The GO can be subsequently reduced in a number of ways by UV irradiation or thermal treatment,⁴ sonolysis,⁵ or chemical treatment with a strong reducing agent such as hydrazine⁶ and is referred to as reduced graphene oxide (RGO). The use of RGO in lithium ion batteries is still in its infancy and may provide a practical and inexpensive way to substantially improve the performance of these electrochemical energy storage devices, serving markets ranging from the long-sought electric vehicle as well as simple applications such as cell phones and laptop computers.

GO is an extraordinarily useful material for the development of composite materials as a result of the oxygen moieties spread throughout the formerly-pristine carbon sheet. These highly electronegative species allow for the stability of the GO colloidal suspension as well as the binding of cations. Binding cationic or organic protonated anions (*i.e.*, acetate) produces GO composites, and subsequently RGO composites that are formed from further chemical processing. The ability to selectively bind cationic materials has led to a swarm of activity surrounding the development of novel GO/RGO-nanoparticle composite materials for a variety of applications. The development of electrodes for lithium ion batteries using the following scheme has produced a number of RGO-metal oxide composites already.⁷⁻¹⁸

Graphene in a Li Ion Battery

Graphene offers many advantages over using typical Li ion battery electrode materials in a standalone fashion.¹⁹ First, the graphene can serve as a binder material, eliminating the use of binding polymer materials such as poly(vinylidene fluoride).²⁰ Second, the high conductivity associated with graphene sheets lends itself to rapid transport of electrons to and from the active material intercalation sites,²¹ particularly given the close physical association of the nanoparticles and the RGO sheets. Also the mechanical strength of the graphene has the potential to absorb some of the expansion and contraction of the anchored nanoparticles during the intercalation and de-intercalation processes,²² which typically lead to mechanical failure of the electrode and performance reduction through the loss of intimate contact of the active material and the conductive carbon black mixed into the electrode material for enhanced conductivity. The electrode can ultimately be pulverized if the expansion is large enough, hence the use of active materials that exhibit small changes upon Li^+ intercalation.

Graphene has also been utilized as a standalone material for Li ion battery anodes in place of traditional graphite and shows some marked improvement in storage and cycling. The storage capacity and cycling ability of graphene was shown to outperform graphite in a number of studies.^{20,23-30} Some have attributed this improvement to the higher surface area achieved in graphene relative to graphite.²⁴ Lithium diffusion

along the edges of graphene following chemical reduction and production of “zig-zag” and “armchair” edge effects was calculated from first principles and supports the experimental findings of better charge/discharge rates and capacity.³¹ The features of RGO (*i.e.*, zig-zag, armchair, creases) were further shown to support enhanced Li^+ intercalation when compared to single-layer graphene where Li^+ repulsion prevented significant intercalation.³² The imperfections achieved in the RGO via reduction of GO provide electronic barriers to Li^+ repulsion effects, which are significant during intercalation into mostly electrically neutral host sites.

The use of carbon families in conjunction with graphene as anode materials was also shown to yield enhanced Li^+ storage. In fact, by controlling the interlayer spacing of the graphene sheets through the use of carbon nanostructures such as fullerenes and carbon nanotubes (CNT), significant improvements were realized beyond the improvement of graphene alone.³⁰ Kinetic barriers may exist in the Li^+ diffusion process into the graphene layers as shown by the over 150% increase in capacity of a graphene anode²⁰ when the current rate was decreased from $50\text{ mA}\cdot\text{g}^{-1}$ to $10\text{ mA}\cdot\text{g}^{-1}$. The improvements realized upon incorporation of the fullerenes and CNT are likely a result of increasing the interlayer spacing and thus decreasing the kinetic barriers to the diffusion of Li^+ into the graphene nanostructures as illustrated in Fig. 1.

The theoretical capacity for graphite anodes is $372\text{ mAh}\cdot\text{g}^{-1}$. When graphene was used as anode material in the aforementioned studies, initial capacities were as high as $1264\text{ mAh}\cdot\text{g}^{-1}$ at a current density of $100\text{ mA}\cdot\text{g}^{-1}$ with some decrease following the buildup of the solid electrolyte interface (SEI).²⁴ Reversible capacities in this study ranged from $718\text{ mAh}\cdot\text{g}^{-1}$ at $500\text{ mA}\cdot\text{g}^{-1}$ and up to $848\text{ mAh}\cdot\text{g}^{-1}$ at $100\text{ mA}\cdot\text{g}^{-1}$ after 40 cycles, almost a 100% increase above the theoretical capacity for graphite. Even graphene nanoribbons have been synthesized for Li ion battery electrodes by unraveling multi-walled carbon nanotubes (MWCNT) in the hopes of limiting the diffusion resistance of the Li^+ into the packed carbon material.²³ Initial capacities up to $1400\text{ mAh}\cdot\text{g}^{-1}$ were recorded with reversible capacities starting near $800\text{ mAh}\cdot\text{g}^{-1}$. However, long-term cycling with the nanoribbons leads to continued loss of capacity, albeit small at $\sim 3\%$ per cycle as shown in Fig. 2, yet suggesting additional work is required for optimization.

Designing Nanocomposites

Graphene-based nanocomposites with SnO_2 ,^{9,11,14,16,18} and other materials such as Sn ,²² Si ,^{33,34} Mn_3O_4 ,^{7,10} Co_3O_4 ,^{8,12} and Ti_5O_{12} ,²¹ have also shown promise as anode materials for Li ion batteries. Figure 1 depicts a common wet-chemical synthesis technique for the complexation of the Mn_3O_4 with RGO, showing that excellent coverage by highly crystalline active materials is possible on RGO. All of the nanocomposites exhibit additional capacity relative to the pure graphene, which is to be expected given the intercalation capability of each of the compounds. With regard to cycling, the SnO_2 exhibits similar stability to that of graphene while the Si capacity decreases considerably with increasing cycle number. The Sn-graphene anode material on the other hand shows exquisite cycling stability, even beyond 100 cycles with an overall high reversible capacity of $508\text{ mAh}\cdot\text{g}^{-1}$. Cu_2O nanocubes were also synthesized *in situ* on GO sheets via complexation of Cu^{2+} with GO¹⁵. The GO was reduced, and the composite anode material was tested and showed initial capacity of $1100\text{ mAh}\cdot\text{g}^{-1}$, although poor cycling renders this material unstable in its current form. Copper compounds will present challenges in that the Cu^+ oxidation state rapidly undergoes disproportionation in most organic solvents.

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Most of the research conducted on graphene nanocomposites for Li ion electrodes has focused on the anode of the battery. Research into graphene-based nanocomposites as cathode materials is fairly mute. Typically in practical application, manganese or cobalt oxides are used as cathode materials, although the nanoparticulate LiFePO_4 has gained much attention recently. In fact, graphene- LiFePO_4 nanocomposites have been prepared recently³⁵ and show improvement by utilizing graphene as an active participant in composite cathode materials. The capacity of the graphene- LiFePO_4 increased from

$\sim 110 \text{ mAh}\cdot\text{g}^{-1}$ to $\sim 160 \text{ mAh}\cdot\text{g}^{-1}$ relative to pure nanostructured LiFePO_4 . Other research supports this finding in showing that a slight coating of carbon over LiFePO_4 led to similar improvements when used as a cathode material.^{36,37} The high surface area of the graphene upon which the nanoparticles can be anchored will likely yield higher capacity composites than carbon coatings, while still serving the purpose of providing enhanced electrical conductivity to the relatively insulating cathode materials such as FePO_4 , MnO_2 , etc.

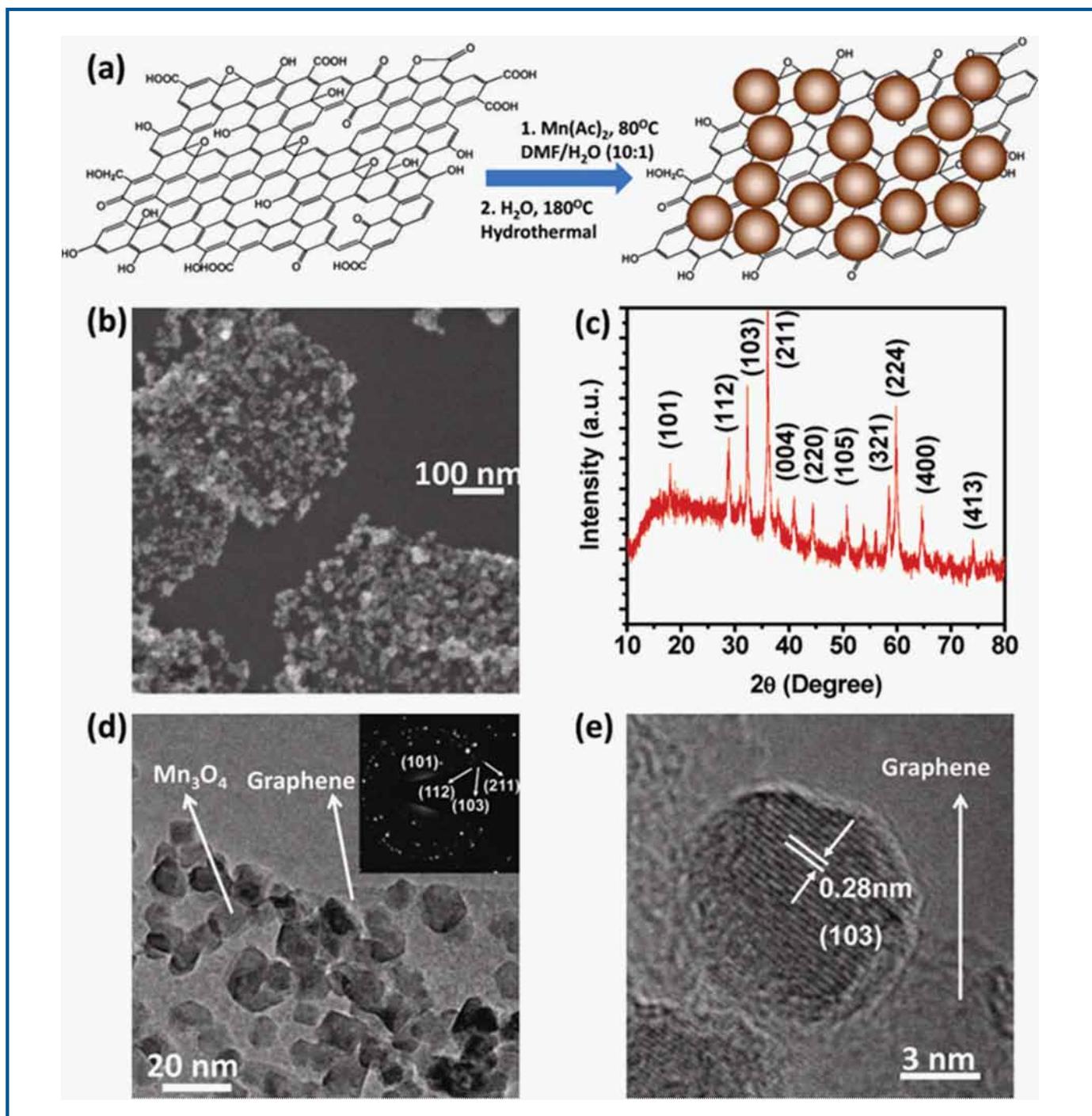


Fig. 1. Mn_3O_4 nanoparticles grown on GO. (a) Schematic two-step synthesis of Mn_3O_4 /RGO. (b) SEM image of Mn_3O_4 /RGO hybrid. (c) XRD spectrum of a packed, thick-film of Mn_3O_4 /RGO. (d) TEM image of Mn_3O_4 /RGO; inset shows the electron diffraction of the Mn_3O_4 nanoparticles on RGO. (e) High-resolution TEM image of an individual Mn_3O_4 nanoparticle on RGO. (From Ref. 7. Reprinted with permission from the American Chemical Society.)

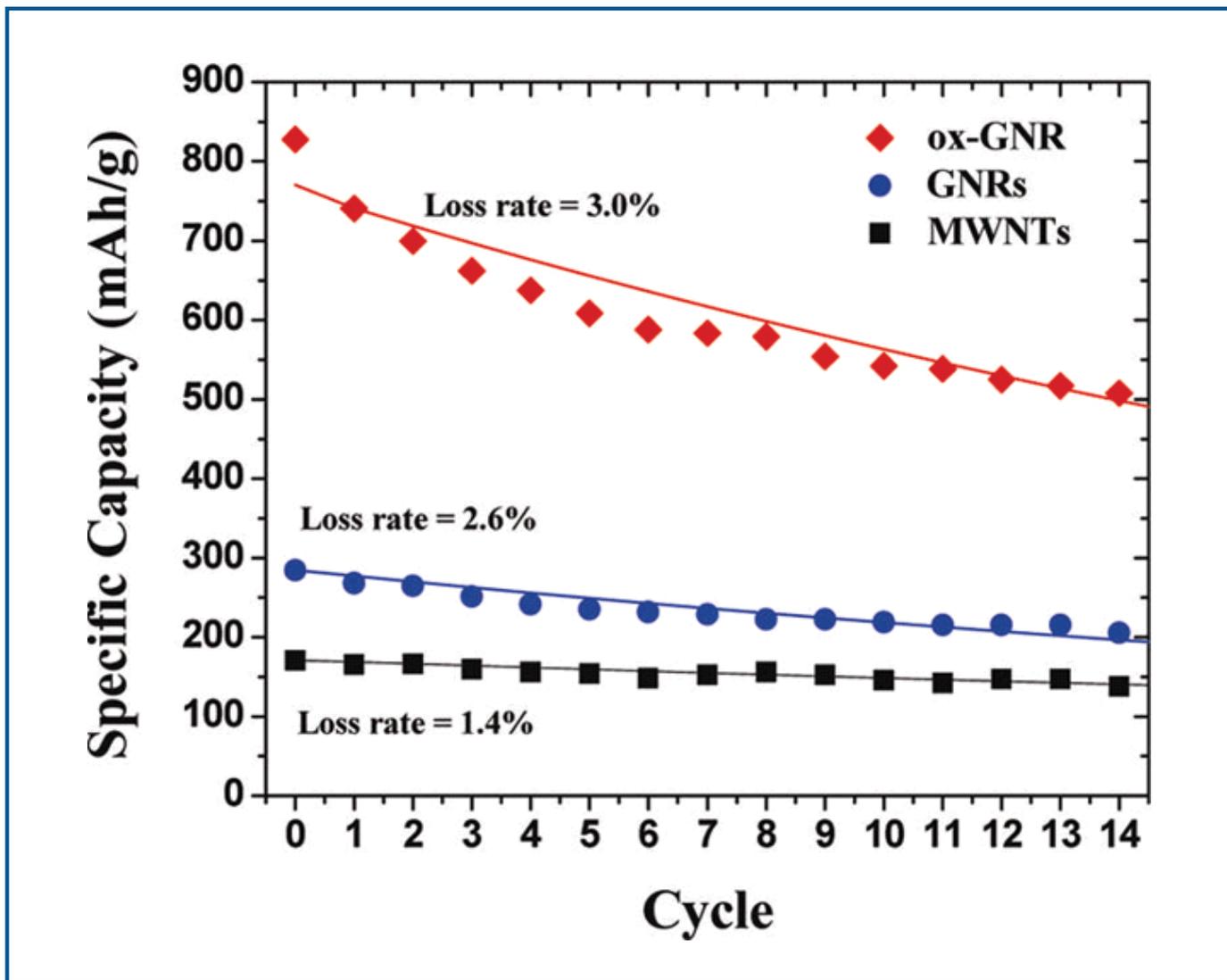


Fig. 2. Cyclability of three different carbonaceous electrode materials. Symbols represent experimental measurements, while bold lines represent values extrapolated at the indicated loss rates. (From Ref. 23. Reprinted with permission from the American Chemical Society.)

Future Challenges

The research effort into the development of Li ion battery cathode materials involving graphene is yet to be exploited fully. The essential problems faced in the overall challenge of constructing viable cathode materials remain in place:³⁸ (1) phase transitions, (2) structural stability, (3) cationic ordering, (4) low conductivity, and (5) excessive solvent/electrolyte reactions beyond typical SEI at the highly-oxidizing electrode surface. Graphene can provide direct support to (2), (4), and potentially (5), and the binding of materials to the graphene sheets may provide synergistic benefits beyond those logically expected. For example by utilizing select synthetic techniques for the production of the graphene nanocomposites such as photochemical reduction coupled with simultaneous binding,^{39,40} nanocomposites consisting of very small particles (~2-5 nm) were nearly embedded into the graphene sheets. Nanocomposite materials with such high surface to volume ratios would be expected to retain mechanical strength upon cycling through the intercalation and de-intercalation processes. Additionally, the metal oxide nanoparticle size will ultimately dictate the interlayer spacing between the graphene sheets similar to that observed with fullerenes and CNT,³⁰ thus providing an opportunity to tune the material for optimal performance of the Li⁺ diffusion and intercalation processes.

Graphene presents unique opportunities to the scientific community through its diverse and varied properties, which show promise to enhance many catalytic, photoelectrochemical, and electrochemical processes. The inexpensive route to RGO from GO and selective binding properties exhibited by the latter open doors to the creation of composite materials for these applications. Synergistic effects are already observed in the multiple facets of graphene-based composites, and lithium ion batteries stand to benefit considerably through further understanding of the interactions of intercalation materials, lithium ions, and graphene.

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