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Better performing composite cathode encompassing graphene and magnesium aluminate for Li–S batteries

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HIGHLIGHTS

- A ternary sulfur composite electrode encompassing graphene and $MgAl_2O_4$ was prepared.
- The migration of polysulfide was successfully reduced by $MgAl_2O_4$ spherical particles.
- The Mg^{2+} offers two Lewis acidic sites and thus confines polysulfides.
- The obtained results are better than those reported earlier with metal–organic frame work—as solid additive.

GRAPHICAL ABSTRACT
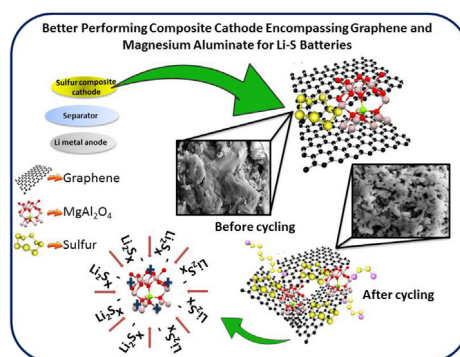
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ABSTRACT

The issues such as low ionic conductivity of sulfur, shuttling of polysulfide intermediates and poor interfacial properties of lithium metal anode with electrolytes hamper lithium–sulfur batteries from commercialization. In order to conquer these issues, numerous attempts have been made by researchers across the world. Herein we introduce a novel ternary composite electrode composed of sulfur, graphene, and magnesium aluminate ($MgAl_2O_4$). Synergistically, each component functions for a specific purpose: the added graphene sheets facilitate for fast electron transfer while $MgAl_2O_4$ provides strong binding sites for trapping polysulfide intermediates. The sulfur active material which resides in this ternary mixture involves in the electrochemical reactions and delivers energy. With this unique architecture the Li–S cell delivered a specific discharge capacity of 1394, 800, 492 and 117 mAhg^{-1} at 0.1, 1, 2 and 5C-rate respectively on its first cycle. The charge–discharge characteristics are found to be better than earlier reports with metal–organic frame work as additive.

1. Introduction

In the last two decades the issues like fluctuation of oil prices, global warming, propelling hybrid electric vehicles and to store surplus electricity from renewable sources (wind mill and solar cells) have accelerated immense research on different battery systems [1–3]. The lithium–ion battery which is widely used to power electronic gadgets (with a specific capacity of $\sim$ 250 mAh g^{-1} and an energy density of $\sim$ 800 Wh kg^{-1}) is insufficient to meet out the requirements for electric vehicles and stationary power grid applications [4,5]. lithium–sulfur battery system, on the other hand, has been identified as an alternative to lithium–ion batteries. Although Li–S system was introduced in 1962 its technological importance is recognized very recently [6]. Several review articles describe

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the fundamental aspects and working principles of lithium–sulfur batteries [5,7–12].

The appealing properties such as high theoretical capacity (1675 mAh g^{-1}), low cost, abundance of sulfur on earth, environmental friendliness, and low operating voltage (2.1 V vs. Li/Li$^+$) qualify lithium Li–S batteries as an alternative system to lithium–ion batteries [13–15]. However, several challenges hamper Li–S system from commercialization. The poor electronic and ionic conductivity of sulfur and sulfur species reduce the specific capacity and rate capability [16,17].

In order to enhance the electronic conductivity of sulfur (S) and solid sulfur species (Li$_2$S$_2$ or Li$_2$S) wrapping/encapsulating of elemental sulfur into carbon matrices has been attempted [18–22]. Besides, the dissolution of polysulphides in the electrolytes and their subsequent migration between electrodes lead to low Coulombic efficiency, high self-discharge and capacity fading eventually [23,24]. The poor interfacial properties of lithium metal anode with electrolytes also deteriorate the performance of lithium–sulfur batteries [25,26].

More importantly, the volume change (approximately 80%) in the sulfur cathode upon cycling is also a major concern [27–29]. Several strategies have been adopted to address these issues. In order to alleviate this issue, sulfur–carbon based nanocomposite electrodes were prepared by simple mixing, direct growth or in-situ carbonization. This procedure not only enhanced the conductivity of sulfur but also prevented volume changes by providing mechanical buffering effect through the pores while cycling [30].

Unfortunately, carbon hybridization is found to be less active in trapping polysulfides due to the weak chemical interaction between the nonpolar carbon and polar polysulfides [31]. Liang and co-workers have significantly enhanced the Coulombic efficiency and cycling stability of Li–S cells laden—with metal oxides and chalcogenides as a strong binder for polysulfides. However, these additives are less conductive than graphitic carbon which drastically reduced the specific capacity and rate capability [32]. Attempts have also been made enhance the cycling performance of Li–S cells with metal–organic frameworks [33,34].

Therefore, in the present study, a ternary composite electrode composed of elemental sulfur, graphene and MgAl$_2$O$_4$ was prepared by mild ball milling and employed as cathode material lithium–sulfur batteries. Our earlier studies demonstrated that spinel MgAl$_2$O$_4$ possesses better electrochemical properties as filler and host for separator than other metal oxides such as Al$_2$O$_3$ and MMT-nanoclay [35,36]. Also noteworthy, that magnesium spinel MgAl$_2$O$_4$ has desirable properties of high melting point (1250 °C), high strength, resistance to chemical attack and low electrical losses. Moreover, between two rows of Mg–ions in (110) plane there is an empty space exists with almost no charge [37]. More importantly, graphene suffers from serious agglomeration and re-stacking upon removal of suspension solvents due to the van der Waals interactions between adjacent sheets, and hence leading to a great loss of effective surface area and thus offers inferior electrochemical properties than expected. The electrochemical properties can significantly enhanced by re-stacking the graphene nanosheets. According to Wu and co-workers [38] the synergistic effect between graphene and metal oxides, metal oxide nanoparticles (MgAl$_2$O$_4$) supported on both side of graphene can serve as a nanospacer to separate the adjacent graphene sheets. The loading of metal oxide fine particles can inhibit or decrease the possibility of serious agglomeration and re-stacking of graphene. In the ternary composite electrode the spherical shaped MgAl$_2$O$_4$ provides binding sites for polysulfide intermediates with Mg^{2+} cite to offer two Lewis acidic sites for Lewis acid interaction while graphene flaks facilitate for fast electron transport and the combination of these two components form a network to store sulfur active material. Here after the sulfur, graphene, sulfur + graphene, sulfur + graphene + MgAl$_2$O$_4$ ternary composite are designated as S, G, SG and SGM respectively.

2. Materials and methods

2.1. Materials

Citric acid, magnesium chloride (MgCl$_2$), aluminium nitrate (Al(NO$_3$)$_3$ $-$9H$_2$O) and ammonium hydroxide were purchased from Aldrich, USA. Elemental sulfur with 99.99% purity was procured from E. Merck, Germany and was stored in an argon filled glove box (MBraun, Germany) to avoid further contamination.

2.2. Synthesis of materials

Citric acid-assisted nanocrystalline MgAl$_2$O$_4$ was synthesized by sol–gel method as reported by us earlier [36]. Briefly; appropriate amounts of MgCl$_2$ and Al(NO$_3$)$_3$ $-$9H$_2$O were dissolved in deionized water and added drop wise, under continuous stirring, into an agitated aqueous solution of citric acid. The metal to chelating agent ratio was fixed as 1:2. Initially the pH (pH metre supplied by Metrohm, Italy) of the solution was around 2. The pH of the solution was maintained between 5.5 and 7 by using ammonium hydroxide. The resultant solution was evaporated at 70–80 °C until a sol–gel solution was obtained. The obtained precursor was calcined at 800 °C for 3 h. Figure S1(a) shows the surface morphology of MgAl$_2$O$_4$ which reveals that the prepared particles are spherical in nature. In Figure S1(b), the diffraction peaks corresponding to (hkl) values (221), (311), (400), (422), (440) indicates the crystalline nature of MgAl$_2$O$_4$. Graphene was synthesized by improved Hummer's method [39]. The prepared graphene possesses a flaky structure as seen in the SEM analysis (Figure S1(c)). Also the XRD peaks shown in Figure S1(d) confirm the formation of graphene. MgAl$_2$O$_4$-graphene-elemental sulfur composite was obtained by mild ball milling (Retsch, USA) of elemental sulfur, MgAl$_2$O$_4$ and graphene in the weight ratio of 70:10:20: for 5 min with 100 RPM. Upon ball milling the resultant composite material was heated at 155 °C in an argon atmosphere for 90 min to impregnate sulfur into the graphene and MgAl$_2$O$_4$ binary mixture. In the same way S–G composite was prepared without MgAl$_2$O$_4$ in order to compare its performance.

2.3. Characterization of materials

The content of sulfur in the cathode material was measured by TG and EDAX analyses. Powder X-ray diffraction patterns were recorded between 10 and 80°(Jeol X-ray diffractometer, model, D/Max 2500) plotted with a nickel-filtered Cu–Kα radiation source. The morphologies of the ternary electrode was examined by a (FE-SEM S-4700, Hitachi, Japan) field-emission scanning electron microscope. Thermo-gravimetric analysis was conducted in the temperature range between 20–600 °C at a heating rate of 5 °C min^{-1} in a N$_2$ atmosphere. The electrochemical impedance spectroscopy (EIS) measurements were carried out (Biologic, France) before and after cycling and also at different depth of discharge (DOD) and depth of charge (DOC) of the Li–S cell. The values of R_{ct}, and R_e were calculated by employing Electrochemical Z fit tool in Biologic software. The ternary composite material was analysed by Fourier Transform-Infrared spectroscopy (FTIR, Thermo NICOLET Corporation, Nexus Model-670) between 400 and 4000 cm^{-1}. The infrared spectra were obtained at ambient temperature with an 8 cm^{-1} resolution. The XPS analysis (Thermo Scientific Model: MULTILAB 2000) was made for the SGM samples after 100 cycles between 100 and 600 eV.