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Increasing the reversibility of Li–O_2 batteries with caterpillar structured α–MnO_2/N–GNF bifunctional electrocatalysts

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ABSTRACT

The high performance of α–MnO_2/NGNF catalyzed air cathode for Li–O_2 battery is reported in this article. The α–MnO_2 nanorods are successfully grown on highly conductive nitrogen doped graphite nanofibers with caterpillar like morphology by a simple hydrothermal technique. The as–prepared α–MnO_2/N–GNF catalyst exhibits better electrocatalytic performance in terms of oxygen reduction and evolution reactions in the air cathode exhibiting comparatively low overpotential. In addition to the low overpotential, α–MnO_2/NGNF catalyzed Li–O_2 battery also show high capacity, reversibility and rate capability. The combined effect of α–MnO_2 and N–GNF for facilitating electrochemical reactions between Li and O_2 is described for improving energy and columbic efficiency of Li–O_2 battery.

1. Introduction

Li–air battery has taken a massive leap forward with increased number of research publications in the past few years. This attention is mainly because of its exceptionally higher gravimetric energy storage density comparable to that of gasoline [1,2]. Yet there are various aspects to be considered to make this technology practically possible. The overall electrochemical reaction of the battery can be expressed as $2(Li^+ + e^-) + O_2 \Leftrightarrow Li_2O_2$; during which oxygen reduction reaction (ORR) takes place on discharge process (forward), followed by the oxygen evolution reaction (OER) on charging (reverse). One of the major problems in Li–air batteries is the formation of undesired discharge products besides Li_2O_2. In many cases the discharge product from oxygen reduction reaction (ORR) on cathode is not only Li_2O_2. There are other products which are also formed that can easily react with the electrolytes to form organic lithium salt degrading the cell cyclability rapidly. Another major problem which hurdles this technology is the very large potential difference between the ORR and OER in cathode resulting in low round trip efficiency [3]. The former problem is being investigated with various suitable electrolytes, while it is hoped that the development of better electrocatalysts can solve the latter by reducing the overpotential and increasing the cyclability of the battery [4,5].

Catalysts are one of the most important materials that influence the charge/discharge process in Li–air batteries. The ORR and OER at the air–cathode of Li–O_2 batteries are important processes which control the overall cell performance [5]. Hence it is necessary to develop efficient ORR and OER bi-functional electrocatalyst. Precious metal catalysts such as Au, Pd, Pt etc., [6–8] and metal oxide catalysts like Fe_2O_3, Co_3O_4 and MnO_2 [9,10] have been investigated as potential catalyst materials that control the performance of oxygen electrodes. Particularly, after the significantly high capacity with α–MnO_2 nanowires catalyst was reported by Debart et al. in 2008 [10], there have been vigorous investigations on α–MnO_2 nanomaterials to optimize the performance. Recently Kang et al. [11] also reported a high capacity Li–O_2 battery with α–MnO_2 nanowires as catalysts with a stable cyclability for 20 cycles with limited depth of discharge. In our previous report, we have reported the high electrocatalytic activity of 3 dimensional α–MnO_2 nanourchins on air cathode. The α–MnO_2 catalyzed electrodes exhibited a stable cycling performance with increased discharge capacity and reduced overpotential [12]. Hu et al. [13] also reported the application of porous manganese oxide nanostructures in Li-O_2 batteries. Even though α–MnO_2 with different structures and morphologies have

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been synthesized and applied as suitable catalysts in Li–O_2 batteries, the catalytic activity is still far below the commercial Pt based catalysts.

The reason for the underperformance could be the low electrical conductivity of manganese oxide nanomaterials. In order to improve the electrocatalytic activity, one of the desirable methods is to combine or grow the α–MnO_2 catalysts on a highly conductive support. Guan et al. [14] optimized the α–MnO_2 catalysts by coating them directly on multi-walled carbon nanotubes. They observed enhanced oxygen reduction and evolution reactions, and improved energy efficiency and cyclability. Yu et al. and others [15–17] have assured that rGO/α–MnO_2 composite can potentially make a good cathode for Li–air batteries and other energy storage devices. They have identified the roles of reduced graphene oxide and other graphene based materials in sustaining relatively high capacities with α–MnO_2 composite electrodes. Chen et al., [18] introduced nitrogen–doped exfoliated graphene and α–MnO_2 nanotube composite as ORR active air cathode material for Li–O_2 battery applications. They observed improved ORR activity of the material due to the addition of superior electronic property of graphene and the defective sites generated by nitrogen doping. Graphite nanofibers (GNF) with its unique properties like high conductivity and decreased impurities are suitable catalyst support which has been investigated intensively for various applications [19–21]. Owing to the large surface area, flexibility, and chemical stability, graphite has always been an excellent substrate to host active nanomaterials. Also, preferred crystallographic orientation of α–MnO_2 can be attained as a result of interaction in the highly ordered GNF substrate [19–21]. But GNF has not yet been utilized as catalyst support for Li–O_2 battery applications to the best of our knowledge even though CNF electrodes can provide gravimetric energies up to 2500 Whkg^{-1} at powers up to 100 Wkg^{-1}, which are among the highest values reported for Li–O_2 batteries to date (including carbon-only and catalyst-containing electrodes) [22].

In this work, we have grown α–MnO_2 nanorods on highly conductive graphite nanofibers (GNF) with caterpillar like morphology for electrocatalytic application. In addition we doped the GNF with nitrogen (N) (here after called as N–GNF) before growing α–MnO_2, because it is well established that incorporation of nitrogen increases the activity by introducing structural defects [23,24]. The as-prepared α–MnO_2/N–GNF nanomaterials were examined for ORR and OER activities in the air cathode of Li–O_2 cell. The α–MnO_2 nanorods grown on N–GNF exhibited high capacity and reversibility with low overpotential. The better performance of Li–O_2 battery with caterpillar shaped α–MnO_2/N–GNF obtained in our experiment is far better than other previous reports [10,15,23].

2. Experimental method

GNF materials were commercially purchased from (Carbon nanomaterial technology, co., Ltd) and doped with nitrogen. We employed the nitrogen doping process that was utilized in our previous report [24] with negligible modification. The α–MnO_2 nanorods were then grown on N–GNF by simple hydrothermal technique [12] based on our mechanistic study on phase and morphology conversion of MnO_2 nanostructures [26]. $KMnO_4$ was mixed with N–GNF under mortar and pestle condition and dispersed the mixture into 30 ml DI water. Later 250 μl H_2SO_4 was added into the solution. Finally hydrothermal treatment was performed at 80 °C for one hour. The as-prepared sample was wash with DI water and dried under vacuum. Thus obtained final product was α–MnO_2/N–GNF nanostructure.

The as–prepared material was characterized by x–ray diffraction spectrum (XRD, X'PERT–MRD, Philips) to identify the phase and crystal structure. The morphology of the prepared composite was analyzed by field emission scanning electron microscopy (FESEM) (S–4700, HITACHI) and transmission electron microscopy (TEM). X–ray photoelectron spectroscopy (XPS) analysis was performed using a thermo scientific Kα x–ray source, which was used to confirm the nitrogen doping in GNF. EDX analysis was utilized to identify the chemical composition of the grown nanostructure. Brunauer–Emmett–Teller (BET) (BEL SORP Bell Japan Inc.) surface area analysis was employed to study the specific surface properties of the synthesized nanocomposite.

For lithium battery studies, the α–MnO_2/N–GNF catalyst and conductive KB carbon were mixed in the ratio of 1:2 with teflonised acetelyn black binder in iso–propyl alcohol and made into a pellet type electrode. The pellet was pressed on Ni mesh current collector, dried over night at 100 °C and employed as cathode. The performance of α–MnO_2/N–GNF catalyst for ORR/OER in Li–O_2 air cathode was evaluated in a Swagelok^{TM} type cells with 1 M LiTFSI (TEGDME) electrolyte and Li anode. The Li–O_2 cell performance was tested galvanostatically in a potential window of 2~4.3 V in a BTS 2004 (JAPAN) battery tester at different current densities (0.1, 0.2 and 0.3 mA/cm^2) in room temperature and 1 atm O_2 atmosphere.

3. Results and Discussion

3.1. Physical properties

Shown in Fig. 1 are the XRD spectra for α–MnO_2, GNF, N–GNF and α–MnO_2/N–GNF, respectively. The synthesized MnO_2 material shows characteristic α–MnO_2 XRD peaks at 2θ (110), (200), (310), (211), (301), (411), (600), (521) and (002), which coincide with JCPDS 44-0141, and GNF material exhibits characteristic carbon peaks around 2θ = 26° corresponding to (002) graphitic planes, as shown in Fig. 1. The α–MnO_2/NGNF shows both the α–MnO_2 and graphite related peaks, which identify the growth of α–MnO_2 over N–GNF. To confirm the doping of nitrogen in N–GNF, XPS spectrum was obtained. The XPS spectrum in Fig. 2(a) shows the presence of N and O in N–doped GNF (N–GNF) by identifying N1s and O1s at binding energies of 397.7 and 533 eV, respectively [25]. EDX elemental analysis clearly given in Fig. 2(b) shows that the surface of α–MnO_2/N–GNF structures are mainly

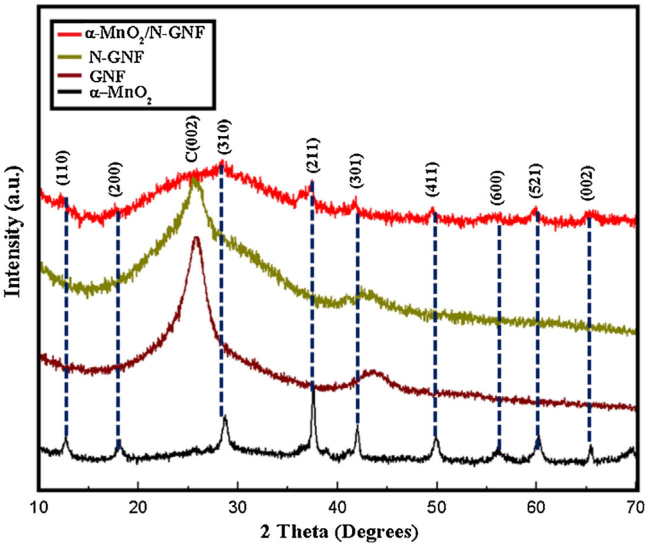

Fig. 1. X–ray diffraction of spectra of α–MnO_2, GNF, N–GNF and α–MnO_2/NGNF nanomaterials.