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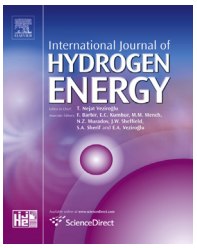

Monodisperse MPd (M: Co, Ni, Cu) alloy nanoparticles supported on reduced graphene oxide as cathode catalysts for the lithium-air battery

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ABSTRACT

Addressed herein is the electrocatalyst performance of the monodisperse MPd (M: Co, Ni, Cu) alloy nanoparticles (NPs) supported on reduced graphene oxide (rGO) for the non-aqueous Li-air battery. MPd alloy NPs were prepared by using a well-established surfactant-assisted organic solution phase protocol comprising the co-reduction of palladium(II) acetylacetonate and $M(acetate)_2$ or $M(acetylacetonate)_2$ by borane-based mild reducing agents in oleylamine. As-synthesized Co_3Pd_7, Ni_3Pd_7 and CuPd NPs have uniform particle size distribution with the average particle size of 3.5, 3.4 and 3.0 nm, respectively. The colloidal MPd NPs were then supported on rGO before their use as cathode catalysts in the non-aqueous Li-air battery. The charge–discharge curves of Li-air electrodes using rGO-CuPd, rGO-Co_3Pd_7 and rGO-Ni_3Pd_7 catalysts were investigated at a current rate of 100 mA g^{-1}. The specific discharge capacities were found as 4407 mA h g^{-1} for rGO-CuPd, 3158 mA h g^{-1} for rGO-Co_3Pd_7 and 2512 mA h g^{-1} for rGO-Ni_3Pd_7. Ex-situ FTIR analyses after the 10 cycle recyclability test revealed that Li_2O_2 is the main component of the discharge products. The lifetime of the cathode electrodes during the first 10 cycles was found to be 100 h for rGO-Co_3Pd_7, 130 h for rGO-CuPd and 180 h for rGO-Ni_3Pd_7. The Ni_3Pd_7 has the highest total capacity of 8175 mA h g^{-1} over the first 10 cycles.

Introduction

Hydrogen has already appeared in our everyday applications as a clean energy vector owing to recent scientific and technological progress in the hydrogen economy [1]. However, hydrogen storage or in a broader context energy storage is considered to be a crucial technology for the advancement of hydrogen fuel-cell power technologies in transportation, stationary and portable applications [2,3]. On the other hand, the hybrid electric and plug-in hybrid electric vehicles are attracting wider attention while energy challenges and environmental problems increasing gradually [4]. Therefore, the rechargable battery technologies are the most promosing

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solutions for energy storage problem. In this respect, lithium-ion batteries have been used in portable electronic devices for almost two decades, but their energy density (150–250 Wh kg^{-1}, on cell level) is limited to be used in electric vehicles and stationary energy storage applications [5]. Recently, lithium-air batteries (LABs) have gained increasing attention as alternate power source for the future owing to their high specific energy density (1000–1500 Wh kg^{-1}, on cell level) that is much greater than that of lithium-ion batteries [6,7]. In general, LABs have a lithium anode, an air cathode and a separator between the anode and carbon-based air cathode. Several technical obstacles must be handled in order to design a rechargeable LAB with the desired energy density and cycle stability [8]. The hurdles associated with the air cathode are the most important ones among those challenges because air cathode has a major role on the performance of LABs. At the cathode of a LAB, the catalytic oxygen reduction reaction (ORR) occurs during the charging process (Eq. (1)) [9]. The resulting Li_2O_2 can be further discharged to form Li_2O via oxygen evolution reaction (OER) (Eq. (2)).

$$2Li + O_2 \leftrightarrow Li_2O_2 \quad E = 3.10\ V \tag{1}$$

$$2Li + Li_2O_2 \leftrightarrow 2Li_2O\ E = 2.72\ V \tag{2}$$

Combining Eqs. (1) and (2), the overall cathode reaction is formed (Eq. (3)).

$$4Li + O_2 \leftrightarrow 2Li_2O \quad E = 2.91\ V \tag{3}$$

The recent studies on LABs have been directed to develop new cathode materials that enhance the OER and ORR efficiencies [10,11]. Up to date, a variety of carbon materials such as mesoporous carbon, carbon nanotubes, carbon fibers and graphene have been tested as the cathode electrode for LABs [12]. Among them, graphene-based systems have attracted a great deal of attention owing to their excellent properties such as high electric conductivity (10^3–10^4 S m^{-1}) and high specific surface area (2630 m^2 g^{-1}) [13]. However, the overall results indicated that the performance of single carbon materials, even graphene-based materials, is not enough for the design of high round-trip efficiency LABs due to the high voltage gap between discharge and charge (>1.5 V) reactions. In this respect, it was proven that the use of electrocatalysts will not only reduce the overpotential of discharge/charge process but also facilitate the ORR and OER at the cathode, which improves the capacity and round-trip efficiency of the LABs (See Table S1 for the various catalysts system tested in Li-air battery). Therefore, the recent studies about LABs have been directed to design and develop electrocatalysts for the air cathode. For instance, Munichandraiah et al. reported an initial discharge capacity of 5230 mA h g^{-1} at a rate of 90 mA $g^{-1}$and a cycle life of 120 cycles in the presence of rGO supported Au nanoparticles (NPs) under the atmosphere of dry-oxygen gas [14]. In this regard, rGO supported Pd catalyst either in monometallic or bimetallic alloy structure in the presence of a nonprecious metal might also be considered for the development of more economical cathode catalysts for the LABs because Pd is less expensive than Au and provide higher capacity compared to other precious metals such as Pt ans Ru at the air cathode [15]. For example, Song and Han reported that CuPd bimetallic NPs demonstrate an outstanding rate capability of about 2000 mA h g^{-1} even at a high current density of 5000 mA g^{-1} under dry-oxygen [16]. However, a literature survey was resulted in no example of rGO-MPd (M: Co, Ni) alloy NPs tested as air cathode catalysts for LABs. Besides various catalyst systems have been tested till now for LABs (See Table S1), new approaches to generate different cathode active materials have been evaluated for the LABs. For instance, Jin et al. [17] reported an initial discharge capacity of 1235 mA h g^{-1} by using the $Ba_{0.9}Co_{0.5}$ $Fe_{0.4}Nb_{0.1}O_3$-δ perovskite as cathode catalysts in nonaqueous Li-air battery. In another study, Wang et al. [18] demonstrated that a mixed metaleion metaleorganic framework (MOF(Fe/Co)) has an excellent bifunctional catalytic activity for the rechargeable aqueous or hybrid lithium-air batteries. As an example to the high capacity Li-air batteries, Gao et al. [19] reported a discharge special capacity of 6587 mA h g^{-1} of carbon at the rate of 0.15 mA/cm^2 with double-layer structure of gas diffusion layer and catalyst layer at the Li-air electrode.

In this study, we report for the first time testing monodisperse MPd (M: Co, Ni, Cu) alloy NPs supported on rGO as cathode catalysts for the nonaqueous LAB. Monodisperse MPd alloy NPs were synthesized by using a surfactant-assisted organic solution phase protocol including the reduction of palladium(II) acetylacetonate ($Pd(acac)_2$) with M(II) acetates ($M(ac)_2$) or M(II) acetylacetonates ($M(acac)_2$) in oleylamine by morpholine borane or borane-tert-butylamine complexes. The MPd NPs were characterized by TEM, XRD and ICP-MS and supported on rGO via liquid self-assembly method before the electrocatalytic tests. The rGO supported MPd NPs (rGO-MPd) were then tested as cathode catalysts in the nonaqueous LAB without any further purification steps. All the rGO-MPd catalysts showed promising performance among which the CuPd provided the highest initial discharge capacity of 4407 mA h g^{-1}, whereas Ni_3Pd_7 has the highest total capacity of 8175 mA h g^{-1} over the first 10 cycles.

Experimental

Materials

Palladium(II) acetylacetonate ($Pd(acac)_2$, 99%), cobalt(II) acetylacetonate ($Co(acac)_2$, 97%), copper(II) acetylacetonate ($Cu(acac)_2$, 99%), nickel(II) acetate tetrahydrate ($Ni(ac)_2.4H_2O$, 97%), oleylamine (OAm, 70%), morpholine borane complex (MB, 95%), borane-tert-butylamine complex (BTB, 97%), 1-octadecene (ODE, 97%), potassium permanganate ($KMnO_4$, >99%), sodium nitrate ($NaNO_3$, >99%), dimethylformamide (DMF, >99%), hexanes (97%), isopropanol (99%), ethanol (99%) and acetone (97%) were purchased from Sigma–Aldrich®. Natural graphite flakes were purchased from Alfa-Aesar®. Hydrogen peroxide (H_2O_2, 30%) and sulfuric acid (H_2SO_4, 95–98%) were purchased from Merck®. All the chemicals were used as received.

Instrumentation

Transmission electron microscopy (TEM) images were obtained by FEI Technai G^2 Spirit BiO(TWIN) at 120 kV. X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex

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