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Nanostructured porous cobalt oxide synthesis from $Co_3[Co(CN)_6]_2$ and its possible applications in Lithium battery

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ABSTRACT

The thermal decomposition and microwave heating of $Co_3[Co(CN)_6]_2$ leads to formation of nanostructured porous cobalt oxide (Co_3O_4). Here, we report $Co_3[Co(CN)_6]_2$ as a novel single source precursor for the synthesis of phase pure Co_3O_4 particles at 650 °C under mixed argon/oxygen atmosphere as evidenced from X-ray diffraction (XRD) patterns. During thermal decomposition, release of gaseous products like CO_2, N_xO_y, $(CN)_2$ facilitate the formation of a highly porous Co_3O_4 whose morphology and particle size distribution were characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) respectively. Porous Co_3O_4 shows high discharge capacity of 1131 mA h g^{-1} with 96% coulombic efficiency against Li/Li^+ reference electrode.

1. Introduction

Cobalt oxide (Co_3O_4) attracts the attention of the materials researchers because of its promising applications in various fields viz., anode material for Li-ion batteries (LIBs) [1], super capacitors [2], gas sensors [3], catalytic processes [4] etc. Co_3O_4 nanoparticles were synthesized through various routes that include the commonly employed oxidative precipitation [5], thermal decomposition [6,7], hydrothermal synthesis [8,9] etc., Synthesis of metal oxides like NiO, Co_3O_4, from single source precursors is a simple approach to make a porous structure for increasing material performance [10,11]. A few examples of single source precursors include $(NH_4)_2Co_8(CO_3)_6(OH)_6 \cdot 4H_2O$ [12], $Co(CO_3)_{0.5}(OH)_{0.1} \cdot 1H_2O$ [7,13], $Co_4(CO)_{12}$ [14], prussian blue [15]. Epple's group have shown that how crystal structure of the precursor dictates the structure and morphology of the resulting products when thermolysis was carried out under moderate temperatures [16,17]. The catalytic activity towards the formation of methanol from synthetic gas ($CO/CO_2/H_2$) was studied using Cu/ZnO catalyst. Surprisingly, catalytic activity was not observed on Cu/ZnO catalysts synthesized from $Cu[Zn(CN)_3]$ whereas the Cu/ZnO synthesized from complex containing ethylenediamine and cyanide as ligands showed 20–30% catalytic activity [17]. These observations highlight the role of the precursor in determining the crystal structure of metal oxides and their catalytic properties. In this work, we present the formation of porous Co_3O_4 from $Co_3[Co(CN)_6]_2$ by both thermal decomposition and microwave synthesis and its application towards Li-ion battery.

2. Results and discussion

2.1. Synthesis and characterization of $Co_3[Co(CN)_6]_2$

The precipitate $Co_3[Co(CN)_6]_2 \cdot 12H_2O$ was obtained by mixing the solutions of cobalt acetate and potassium hexacyano cobaltate (III). The product can easily be identified by its reversible color transitions in hydrated and dehydrated forms. Similar observations were reported in the literature and attributed to the inter conversion of octahedral to tetrahedral co-ordination of Co^{2+} site [18]. The compound was further confirmed by using FT-IR and XRD analysis.

2.2. Phase composition analysis

From TGA results (Fig. S1A), it was observed that the

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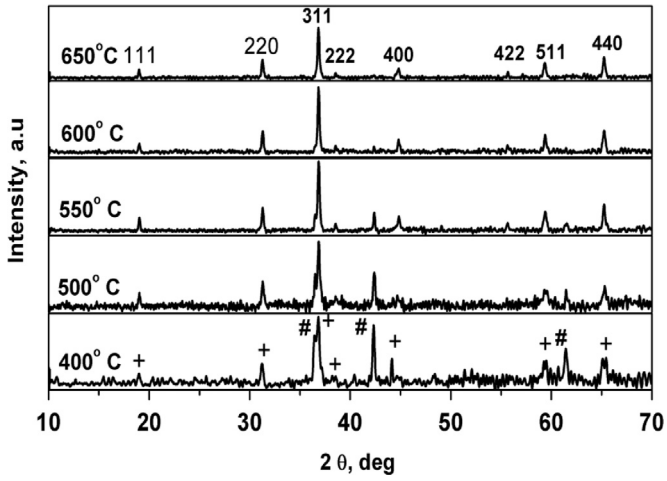

Fig. 1. XRD of cobalt oxide prepared at different temperature. (#) CoO phase and (+) Co_3O_4 phase.

decomposition of cyanide ligands is completed below 350 °C and hence we have synthesized cobalt oxides by fixing the temperature at 400–650 °C in mixed Ar/O_2 atmosphere. XRDs were recorded for the samples prepared from decomposition of $Co_3[Co(CN)_6]_2$ at different temperatures (Fig. 1). From the XRD results, it is confirmed that pure Co_3O_4 (JCPDS no. 01–078–1969) was formed at 650 °C (decomposition temperature) and this temperature, the calculated crystalize size (using Scherrer equation) value (d=8.3 nm) of Co_3O_4 for 311 plane was higher than the value obtained at 400 °C (d=2.1 nm). This imply that The existence of the CoO oxides (JCPDS no: 01–078–0431) phase at a lower temperature may be due to the initial conversion of $Co_3[Co(CN)_6]_2$ partly to cobalt metal and then to metal oxides, viz. CoO and Co_3O_4. This mechanism is suggested because the cyanide ions can act as a reducing agent during thermal decomposition [19]. The two well defined sharp peaks at 574 and 663 cm^{-1} observed [20] in FT-IR spectra (Fig. S1B) were confirmed as due to the Co_3O_4 formation.

2.3. Morphology and particle distribution

Decomposition of $Co_3[Co(CN)_6]_2$, results in a significant change in the mass of the sample. The possible decomposition products in the mixed Ar/O_2 atmosphere are H_2O, CO_2, $(CN)_2$ and N_xO_y [20]. The release of these gaseous products could produce highly porous metal oxide materials and these were confirmed by SEM images of porous Co_3O_4 prepared at different temperatures (shown in Fig.2). We can observe that porous structure in Co_3O_4 was retained irrespective of the temperature but the pore size has shown an increase with temperature (Table ST1). It is clear from the SEM micrographs that the particle size increases with increasing temperature from 400 to 650 °C. This observation is attributed to the aggregation of particles at elevated temperatures. As the temperature increases, the small nanocrystals grow into an interconnected porous structure. Recently, a similar observation is made by Chen et al., during Co_3O_4 formation on calcination of $Co(OH)_2$ [21]. The shape and particle size of the Co_3O_4 was analyzed from TEM studies. Large void spaces present in Co_3O_4 can be clearly seen from SEM image shown in Fig. 2A. It is interesting to know that $Co_3[Co(CN)_6]_2$ is active in the microwave region and hence microwave irradiation can also be followed to decompose $Co_3[Co(CN)_6]_2$. Surprisingly, the microwave assisted synthesis also resulted in the porous cobalt and also existence of cobalt oxide (Fig. 2B) in two different phase's c.a. Co_3O_4 and CoO. Phase pure Co_3O_4 can also be synthesized by optimizing the microwave power and irradiation time. However, more studies are needed to optimize the formation of phase pure Co_3O_4 by microwave heating.

2.4. Electrochemical studies against $Li+/Li^0$

We have also examined the electrochemical behavior of the pure Co_3O_4 as an anode material for Lithium ion battery. Fig. 3A shows the plot of specific capacity (mA h g^{-1}) vs voltage (V vs Li^+/Li^0) obtained for the charge–discharge profiles of the first, fifth and tenth cycles. Fabricated coin cells were cycled at a rate of C/2 from 3.0 V to 0 V. Fig. 3B shows discharge capacity versus cycle number for porous Co_3O_4 at C/2 rate. The discharge capacity of the first cycle was found to be as high as 1131 mA h g^{-1}

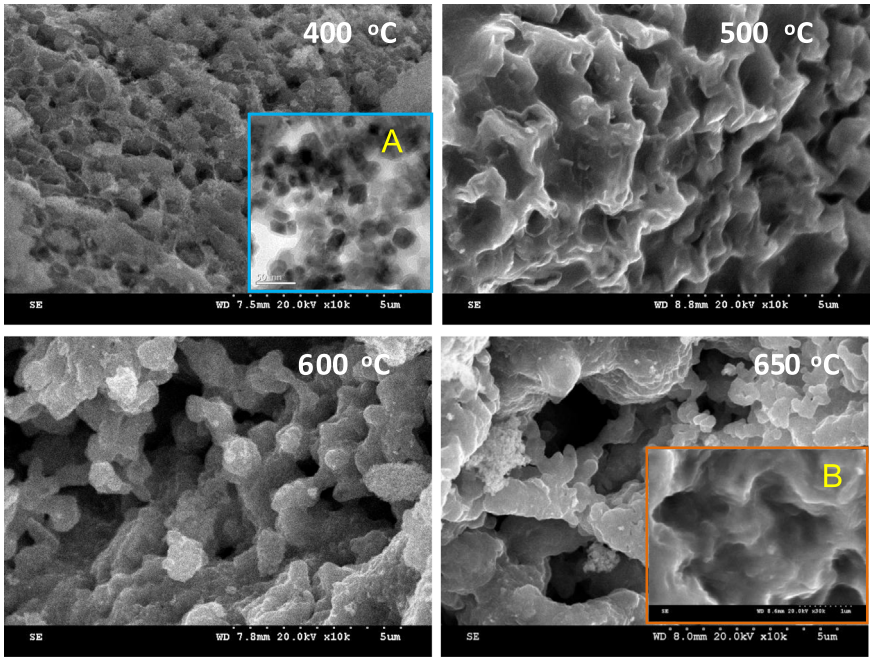

Fig. 2. SEM image of cobalt oxide prepared at different temperatures. Inset figure (A) is TEM image of Co_3O_4 obtained at 650 °C and (B) SEM image of Co_3O_4 obtained from microwave synthesis.

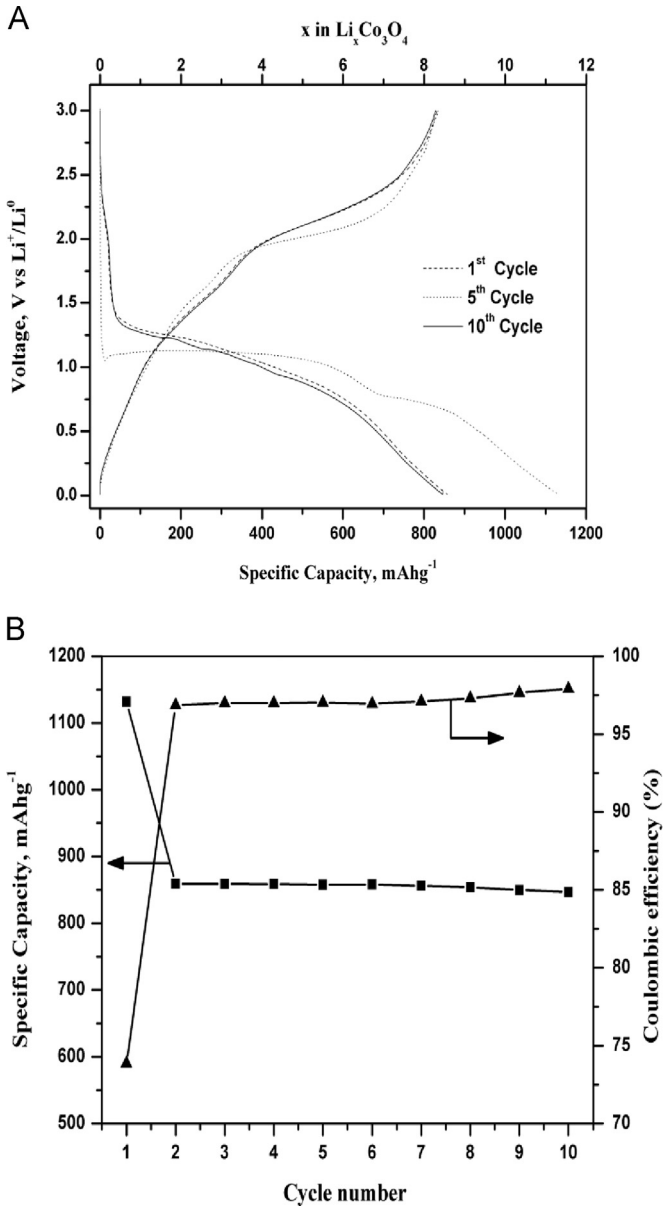

Fig. 3. (A) First, Fifth, Tenth discharge and charge cycle of porous Co_3O_4 at C/2 rate. (B) Discharge capacity versus cycle number for porous Co_3O_4 at C/2 rate.

(corresponding to $x=11.3$). These are generally attributed to the conversion of Co_3O_4 to an intermediate-phase CoO (or $Li_xCo_3O_4$) and then to metallic Cobalt, respectively [1,7]. The sloping region may be due to the formation of a solid electrolyte interface (SEI) which leads to an irreversible capacity loss [4]. On charging, a distinct plateau was seen at 1.95 V which corresponds to the formation of a less lithiated phase ($Li_nCo_3O_4$, $n<x$) with a delivering capacity of 838 mA h g^{-1} (corresponding to $x=8.4$) and 74% coulombic efficiency. Irreversible capacity loss experienced in the first cycle is due to the incomplete decomposition of Li_2O and SEI formation which is not followed in subsequent cycles [9].

3. Conclusions

Here, we have shown a facile route for the synthesis of porous Co_3O_4 from prussian blue analog, $Co_3[Co(CN)_6]_2$. This method for the preparation of nanostructured phase pure metal oxide with high porosity is simple. The formation of the pure Co_3O_4 phase was optimized by varying the temperature between 400 °C and 650 °C. During the thermal decomposition of $Co_3[Co(CN)_6]_2$, a large change in mass and expulsion of gases take place resulting in the formation of a porous cobalt oxide as evident from SEM and TEM images. Co_3O_4 is a promising anode material in Li-ion battery. This porous nano-structured material may help to increase the battery performance by adjusting volume variation occurring during the charge–discharge process. Further possibility of the synthesis of mixed metal hexacynocobaltates with two or three metal ions Ni^{2+} or Mn^{2+} with hexacyanocobaltate ions are expected to lead to the synthesis of newer mixed oxides which may have promising application as advanced energy materials and is in progress.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2015.11.122

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