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# [Co(salen)] derived Co/$Co_3O_4$ nanoparticle@carbon matrix as high-performance electrode for energy storage applications

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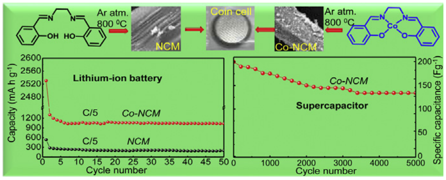
## HIGHLIGHTS

- Co/$Co_3O_4$ nanoparticle@carbon was generated by onepot pyrolysis of [Co(salen)].
- Lithium-ion cell exhibited capacity of 1000 mA h $g^{-1}$ with excellent cycle life.
- Co/$Co_3O_4$@C exhibited specific capacitance of 615 F $g^{-1}$ in KOH with good stability.
- Co/$Co_3O_4$@C can be an electrode for lithium-ion battery as well as supercapacitors.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Cobalt/cobalt oxide nanoparticle-embedded in a carbon matrix was synthesized by one spot pyrolysis of cobalt salen complex [Co(salen)] at 800 °C in an argon atmosphere. The X-ray diffraction studies confirmed the presence of Co and $Co_3O_4$ in the carbon matrix. The SEM and TEM observations showed the homogeneous distribution of the Co/$Co_3O_4$ grains on the carbon matrix. Cyclic voltammograms and galvanostatic charge-discharge studies done on the CR2032 coin cell confirmed that the Co/$Co_3O_4$@-carbon matrix was electrochemically active. A stable specific capacity as high as 1000 mA h $g^{-1}$ has been observed over 50 charge-discharge cycles at C/5 rate. It is believed that the carbon matrix acted both as a spacer to accommodate volume changes during Li intercalation-deintercalation process and also as conductive network leading to the excellent electrochemical performance of the Co/$Co_3O_4$@carbon matrix. Further, supercapacitor studies revealed that a specific capacitance of 615 F $g^{-1}$ at 1 A $g^{-1}$ has been exhibited by the Co/$Co_3O_4$@carbon matrix electrode in 1 M KOH with high Coulombic efficiency (92%) as well as excellent cycling stability for 5000 cycles.

## 1. Introduction

Numerous scientific efforts have been currently devoted to develop high-performance lithium-ion battery (LIB) owing to its attractive features such as high voltage, high energy density, low self-discharge etc. Such admirable qualities of the LIB find its extensive usages currently in portable consumer electronic devices [1,2]. In near future, the LIB will find its extensive usage in plug-in hybrid vehicles (PHEVs), electric vehicles (EVs) etc. The commercial LIB consists of either lithium transition metal-oxide (eg. $LiCoO_2$, theoretical capacity: 270 mA h $g^{-1}$) or $LiFePO_4$ (theoretical

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capacity: 170 mA h $g^{-1}$) as cathode, graphite (theoretical capacity: 372 mA h $g^{-1}$) as anode and the electrolyte is non-aqueous solution of lithium salt (eg. $LiPF_6$) in ethylene carbonate, diethylene carbonate or mixture of them [3,4]. Though the current LIB technology is suitable for low energy and low power consumer electronics, its performance needs to be improved for the implementation in the EVs and large energy storage applications. Specifically, the energy and power densities of the current LIB have to be enhanced to meet the requirements of the traction battery. In this regard, low capacity electrode materials, specifically anode need to be replaced by an efficient alternative anode (high capacity) [5]. It is proposed that metals such as Si, Sn, Ge, Sb, Al [6–12] or metal oxides such as NiO, CoO, FeO [13–17] can be alternative anode which undergoes either alloying or displacement reaction with lithium, unlike the intercalation process in the case of graphite anode. Alloying anodes have severe issues of volume expansion leading to poor cycling and hence less practical.

Currently, transition metal–oxides (TMOs) have been attracted as anode material for LIBs due to their large abundance in the earth crust and low cost. Particularly, CoO (theoretical capacity: 715 mA h $g^{-1}$), $Co_3O_4$ (theoretical capacity: 892 mA h $g^{-1}$) and NiO (theoretical capacity: 718 mA h $g^{-1}$) have been examined as an anode material due to their good electrochemical activity with lithium. These oxides have undergone conversion to metal in reaction with lithium (conversion or displacement mechanism) reversibly. For example, Chen et al., reported CoO as an anode with a capacity of 900 mA h $g^{-1}$ [18]. A discharge capacity of 1120 mA h $g^{-1}$ for CoO nanodisks [19], has been reported by Sun et al.,. Yuan et al., showed initial discharge capacity at 1025 mA h $g^{-1}$ for porous CoO/C composite [20]. Due to less conductivity and poor diffusion of $Li^+$ in these oxides, limited capacity, poor rate capability, and cycle life have been reported. To enhance the performance of the TMOs, a composite consisting of metal oxide and carbon nano-network has been proposed. Recently, Zhu et al., reported ultra-small Sn nanoparticle embedded in N-doped porous carbon as high-performance anode material for LIB. It was shown that the uniform distribution of Sn nanoparticles on the conductive carbon matrix rendered long cycling stability and high discharge rate [21]. Shuai et al., reported cobalt oxide – anchored graphene synthesized by dispersion method as anode for LIB [22]. Du et al., prepared N-doped carbonaceous material containing non–precious metals (M = Co, Fe, Ni) by pyrolysis of respective metal salen complexes and applied as catalyst for Oxygen reduction reaction (ORR) [23]. It was shown that the metals were homogeneously distributed on the carbon matrix. It is believed that the conductive carbon on the metal/metal oxide can facilitate charge and ion transport leading to better electrochemical performance. Thus, in the present work, $Co/Co_3O_4$@carbon matrix was synthesized from metal organic framework by one spot pyrolysis and examined its electrochemical performance for LIB.

For developing advanced energy storage devices which will have high power and energy densities, the current focus is on the generation of hybrid materials for supercapacitor electrodes [24,25]. Due to the attractive electrochemical features of cobalt oxide, recently several works have been devoted on $Co_3O_4$ by tuning its morphology [26] or making its composites [27–29]. The electrochemical performance of cobalt oxide can also be enhanced by having conductive matrix using suitable precursors. Recently, Yan et al., has reported electropolymerized poly[Ni(salen)] as supercapacitor material [30]. In this work, detailed supercapacitor studies were also done on the $Co/Co_3O_4$@carbon matrix. It turned out that the $Co/Co_3O_4$@carbon matrix can be a potential electrode for the high-performance anode in LIBs as well as supercapacitors.

## 2. Experimental

### 2.1. Material synthesis and characterization

The process adopted here for the synthesis of hydrogen salen ligand ($H_2$salen) and cobalt salen complex [Co(salen)] has been reported elsewhere [31,32]. The ($H_2$salen) was synthesized by reacting salicylaldehyde (2.25 ml, 20 mmol) and ethylene diamine (0.7 ml, 10 mmol). The precipitated $H_2$salen ligand was filtered and washed thoroughly with ethanol and dried at 40 °C in vacuum desiccator. The [Co(salen)] was prepared by reacting the $H_2$salen ligand (2.14 mg, 8 mmol) and cobalt acetate (2.02 mg, 8 mmol) in a distilled ethanol. The detailed characterization of the $H_2$salen ligand and the formed [Co(salen)] has been given in the supplementary materials (Figs. S1 and S2). The obtained $H_2$salen ligand and the [Co(salen)] were subjected to one spot pyrolysis at 800 °C under argon atmosphere for 5 h in a tubular furnace. Upon pyrolysis, the salen ligand produced nitrogen-doped carbon matrix hereafter referred as *NCM*, while the decomposition of the [Co(salen)] yielded $Co/Co_3O_4$ nanoparticles–embedded in nitrogen-doped carbon matrix referred as *Co-NCM*. The obtained *NCM* and the *Co-NCM* samples were characterized by X-ray diffraction studies (Bruker D8 advance Da vinci or Rigaku Ultima IV) using $CuK_\alpha$ radiation, Raman spectroscopy (Witec Confocal Raman instrument CRM200 with Ar ion laser 514.5 nm), Fourier transformed infra-red (Nicolet 6700) spectroscopy, Field–emission scanning electron microscope (FE–SEM, carl Zeiss SUPRA55VP) and transmission electron microscope (TEM Technai-20 $G_2$ microscope). The XRD data were collected in the 2θ range from 5 to 80° at a scan rate of 1° $min^{-1}$ with a step size of 0.002°. The thermal analysis of *Co-NCM* sample was done in the temperature range of 30–1000 °C in air at 10 °C $min^{-1}$ scan rate by using thermal gravimetric analyzer (TG-DTA-Q 600 SDT).

### 2.2. Electrochemical characterization

The electrochemical performances of the *NCM* and the *Co-NCM* samples were evaluated by fabricating CR2032–type coin cells. The working electrode was prepared by mixing active material (*Co-NCM* or *NCM*), super P carbon and polyvinylidene (PVDF) binder in a weight ratio of 70:20:10 wt%. The N-methyl-2-pyrrolidone (NMP) was used as solvent to make slurry. The slurry thus prepared was coated on the Cu foil (9 μm thickness) by means of doctor blade technique and dried at 100 °C for 12 h under vacuum. The estimated mass of active material loading on the Cu foil was 2 mg $cm^{-2}$. The coin cells were assembled in an Ar-filled glovebox (M Braun) using Li disc as the counter electrode. A Celgard® was used as separator and 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (2:1:2 in volume) was used as the electrolyte. The cyclic voltammetric (CV) studies were carried out on the coin cell in the potential range of 0.01–3.0 V at a scan rate of 0.1 mV $s^{-1}$. The galvanostatic charge-discharge cyclings were done on the coin cells at each of C/5, C/2, 1C, 2C, 3C, 5C, 10C, and 25C current rates. All the electrochemical experiments were done using Biologic multichannel battery testing workstation (VMP3Z) at room temperature. The electrochemical impedance studies were performed on the coin cell in the frequency range of 400 kHz –50 mHz by using the same electrochemical workstation.

Further, the supercapacitor studies of the *NCM* and the *Co-NCM* samples were recorded in three electrode configuration containing the *NCM* or the *Co-NCM* as a working electrode, Platinum (Pt) as a counter electrode (1 cm × 1 cm) and Ag/AgCl as a reference electrode. The working electrode was fabricated by pasting the slurry on nickel foam (NF) (1 cm × 1 cm) and dried at 80 °C for overnight. The estimated mass of active material loading on the NF was