



## High energy and power density asymmetric supercapacitors using electrospun cobalt oxide nanowire anode



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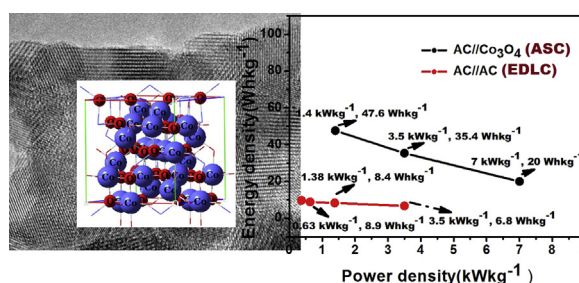
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### HIGHLIGHTS

- Asymmetric supercapacitors were fabricated with electrospun  $\text{Co}_3\text{O}_4$  nanowires and activated carbon.
- Exhibited six fold higher energy density compared to commercial EDLC with no lowering of power density.
- Showed good cycling behaviour with ~97% retention in  $C_s$  at the end of 2000 cycles.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Electrochemical materials are under rigorous search for building advanced energy storage devices. Herein, supercapacitive properties of highly crystalline and ultrathin cobalt oxide ( $\text{Co}_3\text{O}_4$ ) nanowires (diameter ~30–60 nm) synthesized using an aqueous polymeric solution based electrospinning process are reported. These nanowire electrodes show a specific capacitance ( $C_s$ ) of ~1110  $\text{F g}^{-1}$  in 6 M KOH at a current density of 1  $\text{A g}^{-1}$  with coulombic efficiency ~100%. Asymmetric supercapacitors (ASCs) ( $C_s$  ~175  $\text{F g}^{-1}$  at 2  $\text{A g}^{-1}$  galvanostatic cycling) are fabricated using the  $\text{Co}_3\text{O}_4$  as anode and commercial activated carbon (AC) as cathode and compared their performance with symmetric electrochemical double layer capacitors (EDLCs) fabricated using AC ( $C_s$  ~31  $\text{F g}^{-1}$  at 2  $\text{A g}^{-1}$  galvanostatic cycling). The  $\text{Co}_3\text{O}_4$ //AC ASCs deliver specific energy densities ( $E_s$ ) of 47.6, 35.4, 20 and 8  $\text{Wh kg}^{-1}$  at specific power densities ( $P_s$ ) 1392, 3500, 7000 and 7400  $\text{W kg}^{-1}$ , respectively. The performance of ASCs is much superior to the control EDLCs, which deliver  $E_s$  of 9.2, 8.9, 8.4 and 6.8  $\text{Wh kg}^{-1}$  at  $P_s$  358, 695, 1400 and 3500  $\text{W kg}^{-1}$ , respectively. The ASCs show nearly six times higher energy density (~47.6  $\text{Wh kg}^{-1}$ ) than EDLC (8.4  $\text{Wh kg}^{-1}$ ) without compromising its power density (~1400  $\text{W kg}^{-1}$ ) at similar galvanostatic cycling conditions (2  $\text{A g}^{-1}$ ).

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## 1. Introduction

Energy storage devices are increasingly popular nowadays due to wide popularity of multifunctional hand-held electronic devices and hybrid/plug-in electric vehicles [1]. Secondary lithium ion

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batteries (LIB) and supercapacitors (SCs) are two popular protocols for energy storage devices because they are rechargeable, could be produced in diverse design with light weight and flexibility, and are easy to manufacture. The LIB provides high energy density ( $E_S$  ~150–200 Wh kg<sup>-1</sup>) but at the expense of cycle life (<10<sup>3</sup> cycles) and power density ( $P_S$  ~0.5–1 kW kg<sup>-1</sup>); whereas SCs have higher  $P_S$  (2–10 kW kg<sup>-1</sup>) and longer cycle life (10<sup>4</sup>–10<sup>6</sup> cycles) but their  $E_S$  is much lower (<5 Wh kg<sup>-1</sup>) [2–6]. Supercapacitors are of two types based on the energy storage mechanism, viz. (i) electrochemical double layer capacitors (EDLCs) in which a non-faradic charge accumulation occurs at a porous electrode–electrolyte interface; and (ii) pseudocapacitors (PCs), which is based on a faradic reaction at the electrode–electrolyte interface. Allotropes and polymorphs of carbon are choice to build commercial EDLCs whereas PCs are built from ceramic nanostructures and conducting polymers. Recent reviews on supercapacitors are published elsewhere [5,7–9]. Commercial EDLCs suffer from lower  $E_S$  which prevent them from large scale industrial applications. Therefore, unifying high  $E_S$  and  $P_S$  in SCs is an elusive issue.

The  $E_S$  and  $P_S$  are related through.

$$\left. \begin{aligned} E_S &= \frac{1}{2} C_S V^2; \\ P_S &= \frac{E_S}{\Delta t} \end{aligned} \right\} \quad (1)$$

where  $C_S$  is the specific capacitance,  $V$  is the maximum achievable voltage, and  $\Delta t$  is the discharge time of a SC. According to Eq. (1), there are two ways to enhance the  $E_S$ . One way is to use novel electrode material with high  $C_S$ , such as PC materials and the other is to broaden the cell voltage. Therefore, materials that offer higher  $C_S$  and  $V$  are preferred as a SC electrode for high  $E_S$  and  $P_S$ .

A high specific surface area of the electrode material to enable a large electrode–electrolyte interface for efficient redox reaction, high electrical conductivity to enable high rate charging and discharging, and availability of a range of energy states in the host material are the properties of a material to be selected as electrode in PCs. Although PCs have up to 100 times higher  $C_S$  than that of EDLCs their cycle life are relatively lower (<10<sup>4</sup>) because charge transfer process between the electrode–electrolyte interface in the former is relatively irreversible than the charge accumulation at the interface in the later [10]. Owing to its desirable electrochemical

properties for delivering high  $C_S$ , cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) gained considerable attention as a PC electrode [11–16]. Theoretically Co<sub>3</sub>O<sub>4</sub> would deliver  $C_S$  of ~3560 F g<sup>-1</sup>, considering its redox potential ( $\Delta E$ ) at ~0.5 V, which is much higher than that of widely studied hydrated ruthenium oxide (RuO<sub>2</sub>·nH<sub>2</sub>O) (~2200 F g<sup>-1</sup>) and MnO<sub>2</sub> (~1360 F g<sup>-1</sup>) [13,17]. Many efforts are made to optimize Co<sub>3</sub>O<sub>4</sub> morphologies and it's composite with carbon structures/metal to enable high  $C_S$  and cycling stability [16]; a summary of which is in Table 1. The  $C_S$  of Co<sub>3</sub>O<sub>4</sub> nanoparticles are much lower [18,19], typically <10% of the theoretical value, except the hydrothermally grown ones [20]. Although addition of graphene or carbon nanotubes could enhance the conductive properties of the electrode [21] a composite of these carbon structures with Co<sub>3</sub>O<sub>4</sub> also did not improve the  $C_S$  of the resulting electrodes [22–24]. Table 1 clearly shows that one-dimensional (1D) morphologies and flowers of Co<sub>3</sub>O<sub>4</sub> show remarkably higher  $C_S$  [14,15,17].

The improved electrochemical performances of the electrodes using 1D structures are expected to arise from anisotropic charge transport properties; and therefore, they are of considerable importance as PC electrodes and LIB [25]. Among the many techniques for forming 1D morphologies, electrospinning is a simple and versatile technique for producing 1D nanostructures and membranes for many engineering applications including filtration, healthcare, and energy [26,27]. In the electrospinning technique, an organic polymeric solution injected through a syringe needle is spun by an electric field (~10<sup>5</sup> V m<sup>-1</sup>) and is collected on a surface. However, evaporation of large volume of organic solvents during electrospinning have adverse environmental effects; this drawback could be removed by greener processes employing aqueous polymeric solutions.

For a given pseudocapacitive electrode, the  $V$  could be widened by choosing an electrolyte with much different electrochemical potential than the electrode material [11,28,29]. Operating cell voltage as high as 2.7 V is achieved by organic electrolytes and 3.5 V by ionic liquids [30]. However, high cost and toxicity, low conductivity, flammability, and stringent device fabrication requirements in air free atmosphere prevent them from using in large scales. Otherwise, aqueous electrolytes are environmentally benign and easy to handle but suffer from narrow operation voltage window (<1 V; theoretical stability window 1.23 V) [31]. This drawback could be eliminated by fabricating hybrid or asymmetric supercapacitors (ASCs) by combining a PC anode and an EDLC cathode

**Table 1**  
Summary of research describing the electrochemical properties of the Co<sub>3</sub>O<sub>4</sub> electrode.

Morphology	Method of synthesis	$C_S$ (F g <sup>-1</sup> )	$C_S$ retention (cycles)	Current density	Electrolyte	Ref.
Co <sub>3</sub> O <sub>4</sub> nanowire	Ammonia exploration	922	95% (5000)	2 A g <sup>-1</sup>	1 M KOH	[15]
Ultra layered	Homogeneous precipitation	548	99% (2000)	8 A g <sup>-1</sup>	1 M KOH	[12]
Co <sub>3</sub> O <sub>4</sub> /graphene Nanosheets	Ultra sonication	341	89% (1000)	10 mV s <sup>-1</sup>	6 M KOH	[23]
Net like Co <sub>3</sub> O <sub>4</sub>	Solvothermal	1063	91% (1000)	10 mA cm <sup>-2</sup>	6 M KOH	[53]
rGO/Co <sub>3</sub> O <sub>4</sub>	One step hydrothermal	263	92% (1000)	0.2 A g <sup>-1</sup>	2 M KOH	[24]
Hollow Co <sub>3</sub> O <sub>4</sub> boxes	Re-crystallization	278		0.5 A g <sup>-1</sup>	3% KOH	[54]
MWCNT/Co <sub>3</sub> O <sub>4</sub>		200.9			1 M KOH	[22]
Co <sub>3</sub> O <sub>4</sub> nanoparticles	Hydrothermal	928	93% (3000)	1.2 A g <sup>-1</sup>	2 M KOH	[20]
Co <sub>3</sub> O <sub>4</sub> /graphene	In situ solution	478		5 mV s <sup>-1</sup>	2 M KOH	[55]
Co <sub>3</sub> O <sub>4</sub> nanoparticle	Microwave assisted	519	99 (1000)	0.5 A g <sup>-1</sup>	2 M KOH	[18]
Nanoforest	Cathodic co deposition	2.04 F cm <sup>-2</sup>	84% (1500)	5 mV s <sup>-1</sup>	2 M KOH	[56]
Porous Co <sub>3</sub> O <sub>4</sub>	Solid state thermolysis	150	100% (3400)	1 A g <sup>-1</sup>	2 M KOH	[57]
Co <sub>3</sub> O <sub>4</sub> nanotubes	template	574	95% (1000)	0.1 A g <sup>-1</sup>	6 M KOH	[58]
Nanoplate/graphite sheet	Two step method	337.8	93% (1000)	0.2 A g <sup>-1</sup>	6 M KOH	[59]
Co <sub>3</sub> O <sub>4</sub> nanowire	Reflux method	336	98% (400)	1 A g <sup>-1</sup>	6 M KOH	[60]
Graphene nanosheets/Co <sub>3</sub> O <sub>4</sub>	Microwave assisted method	243.2	96% (2000)	10 mV s <sup>-1</sup>	6 M KOH	[16]
Hollow nanowires	Hydrothermal	599	91% (7500)	2 A g <sup>-1</sup>	1 M KOH	[14]
Thin film	Spray pyrolysis	74	100% (1000)	5 mV s <sup>-1</sup>	2 M KOH	[61]
Nano flower	Solvothermal	1936	78% (100)	0.2 A g <sup>-1</sup>	6 M KOH	[17]
Nanoparticles	Plasma spray	162	72% (1000)	2.75 A g <sup>-1</sup>	6 M KOH	[19]
Co <sub>3</sub> O <sub>4</sub> nanowire	Electrospinning	1110	98% (2000)	1 A g <sup>-1</sup>	6 M KOH	This work

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