



# Binder free, porous and nanostructured Co<sub>3</sub>O<sub>4</sub> anode for Li-ion batteries from solution precursor plasma deposition

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## ABSTRACT

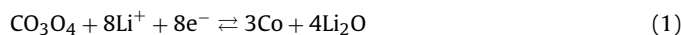
Increasing demand for high energy density in Li-ion batteries has fueled intensive efforts for the search of high specific capacity anode materials to replace the carbon anodes. Among transition metal oxides, nanostructured Cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) was found to be one of the better anode materials for Li-ion batteries. However, the processing routes employed so far have been able to produce different kinds of nanostructured Co<sub>3</sub>O<sub>4</sub> powders, which then require further processing to obtain battery electrodes. Here, we propose a single step and industrial scale solution precursor plasma technique to develop nanostructured, porous and flexible Co<sub>3</sub>O<sub>4</sub> electrodes directly on current collectors. In this process, an aqueous solution precursor comprising of cobalt acetate is fed into a plasma plume to form nanostructured Co<sub>3</sub>O<sub>4</sub> particles, which are then deposited on a current collector. These electrodes are binder and carbon free, and their microstructures revealed nano particulate structure with porosity. Phase, crystallinity and microstructures of the Co<sub>3</sub>O<sub>4</sub> films were investigated by X-ray diffraction, Differential scanning calorimetry–Thermogravimetry (DSC–TGA), Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM). Electrochemical characterization indicated an average cell voltage of ~1.0–1.25 V against Li electrode with specific discharge capacities close to the theoretical value (~890 mAh g<sup>-1</sup>).

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## 1. Introduction

Rechargeable Li-ion batteries are very promising power sources for different applications ranging from small scale microelectronic devices to hybrid electric vehicles because of high energy density and long cycle life [1–3]. But, their energy density is limited by specific capacity of the electrodes used in the cell. Carbon anodes have been in use in Li-ion batteries since their commercialization because of very low potential of carbon with respect to the cathode materials. However, limited specific capacity of carbon (~372 mAh g<sup>-1</sup>), and increasing global demand for high energy density Li-ion batteries for automobile and other large scale applications has been driving the researchers to search for alternative anode materials. Although different material systems have been proposed for anodes [4], the most important challenge in all of them is maintaining the structural integrity over many charge–discharge cycles. Also, the life span of these anode materials is limited due to alloying with Li [4–10]. In the year of 2000, discovery by Tarascon et al. [11] has opened up new opportunities for transition metal oxides as anode materials in Li-ion batteries. However, operating

mechanism of these materials is quite different from the regular Li-ion intercalation mechanism. Among various transition metal oxides, Co<sub>3</sub>O<sub>4</sub> has attracted more attention because of high capacity (~890 mAh g<sup>-1</sup>) and cyclability. The electrochemical interaction of Co<sub>3</sub>O<sub>4</sub> with Li (or Li based cathode compounds) follows the reaction shown below [12], and the Li<sub>2</sub>O formed in this process behaves as an electrochemically active material in the reverse reaction.



Usually, nanostructured electrodes with porosity are desired for enhanced electrochemical reaction kinetics as they provide huge surface area, reduced mass and charge diffusion distances along with added freedom for volume change. There has been extensive research going on to develop nanostructured Co<sub>3</sub>O<sub>4</sub> anodes. Different processing techniques, including wet chemical processes [13–18], solid state syntheses [19], hydrothermal, vapor based and microwave methods [20–24], have been adopted to tailor the structures of Co<sub>3</sub>O<sub>4</sub> and thereby the electrochemical properties. But, most of these techniques need either longer processing times or expensive techniques to synthesize the nanostructured powders of Co<sub>3</sub>O<sub>4</sub>. Consequently these powders require multi-step processing, such as mixing with binder, solvent and additives, then coating machines to spread them on metal foils, and calendaring the coated foils to get uniform thickness etc. [25]. Thus the electrode and battery manufacturing process becomes very time intensive and

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**Fig. 1.** Solution precursor plasma deposited flexible  $\text{Co}_3\text{O}_4$  electrode on a stainless steel sheet (SS304) current collector.

expensive. On the other hand, few research groups [9,16,26–32] have concentrated on developing self supported nanowire arrays of anode materials (e.g.,  $\text{Co}_3\text{O}_4$ , Si etc.) directly on a current collector with or without template assistance. But, the synthesis techniques employed by these groups were again time consuming and less attractive for large scale production. Therefore, manufacturing of nanostructured anodes along with cost reduction is very vital from the commercial application point of view.

Here, we report rapid processing of  $\text{Co}_3\text{O}_4$  electrodes using an industrial scale solution precursor plasma deposition route. This approach makes use of a solution precursor comprising water dissolved cobalt acetate to synthesize bulk scale, nanostructured, porous and flexible  $\text{Co}_3\text{O}_4$  electrodes (see Fig. 1) in ambient conditions. It is also capable of developing electrode films/coatings on complex shapes. During the synthesis process, solution precursor is fed through an atomizer into the plasma plume, which will then undergo accelerated thermo-chemical conversion to form fine  $\text{Co}_3\text{O}_4$  phase particulates. Thus converted  $\text{Co}_3\text{O}_4$  particles will propel toward the substrate/current collector to form electrode films (thickness  $\sim 10$ – $15 \mu\text{m}$ ). Characterization of these anodes in terms of microstructure and electrochemical performance are discussed in the forthcoming sections.

## 2. Experimental procedure

Solution precursor was prepared by dissolving 0.2 mol of cobalt acetate tetrahydrate (98% pure, Alfa Aesar, USA) in 1000 ml of deionized water. For complete dissolution of cobalt salt, solution was stirred for half an hour using a magnetic stirrer. A modified 100HE plasma gun (Progressive Technologies Inc., Grand Rapids, MI, USA) was used for depositing  $\text{Co}_3\text{O}_4$  films on a 25  $\mu\text{m}$  thick stainless steel (304 SS, McMaster Carr Inc., USA) sheet (current collector). An axial liquid atomizer was used to feed the solution precursor into the plasma plume. Spray parameters employed for deposition of  $\text{Co}_3\text{O}_4$  films are shown in Table 1.

Phase and crystallinity of all the materials were determined from X-ray diffraction (XRD) studies conducted using a Rigaku Miniflex X-ray diffraction machine with a  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5402 \text{ \AA}$ ). DSC–TGA experiments were performed on SDT Q600 by heating the samples from room temperature to  $1200^\circ\text{C}$  in air with a ramp rate of  $20^\circ\text{C min}^{-1}$ . Surface and bulk microstructures were examined using SEM (Hitachi 2600-N) and TEM (Hitachi HT 7700), respectively. The samples for TEM studies were prepared following drop-cast method using scraped powders of  $\text{Co}_3\text{O}_4$  films.

**Table 1**  
Solution precursor plasma spray process parameters.

Parameter	Value
Power (kW)	75
Voltage (V)	235
Current (A)	230
Primary gas ( $\text{m}^3 \text{h}^{-1}$ ) (argon)	4.89
Secondary gas ( $\text{m}^3 \text{h}^{-1}$ ) Nitrogen and hydrogen	2.6 and 2.96
Standoff distance (mm)	115
Feed rate ( $\text{ml min}^{-1}$ ) (solution precursor)	45
Atomizing gas (kPa) (compressed air)	182.36
Cooling gas (kPa) (compressed air)	344.73
Material deposition density	$\sim 3.8$ – $4 \text{ mg cm}^{-2}$

Electrochemical characterization was done on Biologic VMP3 analyzer using coin cell assembly.  $\text{Co}_3\text{O}_4$  half cells were prepared in a glove box (Ar atmosphere) with electrolyte (1.5 M  $\text{LiPF}_6$  dissolved in Ethylene carbonate (EC):Dimethyl carbonate (DMC) – 1:2 solution), Celgard 2500<sup>TM</sup> separator and Li counter electrode. All the half cells were assembled in 20 mm diameter coin cells (CR2032) and then crimped. Testing of the coin cells was done by placing them in a stainless steel cell (MTI Corporation).

## 3. Results and discussion

### 3.1. Synthesis and phase analysis

Fig. 2 shows a schematic of solution precursor plasma deposition technique used for the synthesis of  $\text{Co}_3\text{O}_4$  anodes in the present research. As shown in Fig. 2, the solution precursor is atomized by compressed air in the atomizer and enters into plasma plume as fine droplets. Then the high temperatures of plasma plume accelerate the thermo-chemical conversion of the solution precursor droplets into  $\text{Co}_3\text{O}_4$ , which eventually deposit on the stainless steel (SS304) substrate, i.e., current collector. Fig. 3 shows an SEM image of the  $\text{Co}_3\text{O}_4$  anode developed following this approach. Crystallinity and phase structure of the as-deposited films were determined by X-ray diffraction studies, which are shown in Fig. 4 along with the X-ray diffraction pattern of commercial  $\text{Co}_3\text{O}_4$  powders. These studies confirm cubic phase and polycrystalline nature of the  $\text{Co}_3\text{O}_4$  anode films. It is evident from the literature [33–35] that formation of  $\text{Co}_3\text{O}_4$  phase during thermo-chemical conversion of cobalt acetate tetrahydrate (CATH) could be dependent on several factors; for example, the atmospheric conditions employed. According to Mohamed et al. [33], dissociation of CATH at high temperatures ( $>400^\circ\text{C}$ ), and especially in presence of air, can result in the formation of  $\text{Co}_3\text{O}_4$  phase. Otherwise, it could lead to the formation of CoO or metallic Co phases in  $\text{N}_2$  and  $\text{H}_2$  atmospheres, respectively [34,35]. In the plasma deposition approach, the thermo-chemical conversion of solution precursor and deposition of the anode films is usually carried out in ambient air, and therefore, formation of  $\text{Co}_3\text{O}_4$  is quite plausible. However, the extent of thermo-chemical conversion of solution precursor droplets is dependent on several process parameters; such as the temperature of the plasma plume, size/mass of the atomized droplets, time of retention for the droplets within the plasma plume, and/or velocity of the droplet injection. In fact, all these parameters are interdependent, because the velocity of injection can limit the droplet size in thermo-chemical conversion process by affecting the total time of retention in the plasma plume. Small droplet size is preferred for rapid thermo-chemical conversion, and the size of the droplets during atomization process can be tailored by varying the pressure of compressed air as well as the flow rate of the solution precursor. But, the pressure of atomization gas (compressed air) can also act together with the velocity of the plasma jet and control the time of retention. Hence, these three parameters are very critical to achieve

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