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ENHANCED ELECTROCHEMICAL PERFORMANCE IN Al INCORPORATED Co_3O_4 BASED ELECTRODE MATERIALS

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Cobalt oxide based electrode materials are now widely used in rechargeable batteries. In this research work, Al incorporated Co_3O_4compositionswere chemically synthesized to study the effect of *Al* incorporation content on electrochemical performance of host Co_3O_4. Structural analysis was carried out by X-ray diffraction to observe the crystal structure and phase stability. Lattice constant, lattice strain, crystallite size, and cell volume were precisely calculated. Morphology and elemental compositions were extracted using field emission scanning electron microscopy and energy dispersive X-ray spectroscopy, respectively. Fourier transform infrared spectroscopy exhibit the *O-Al-O* and *O-Co-O* and *Al-O* bonding and with increasing the concentration of Al, the vibrational peaks of *Co-O* become sharper. Enhanced electrochemical performance as evident by cyclic voltametry was obtained in compositions with higher Al content.

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1. Introduction

In recent years, there has been an appreciable advancement in energy storage materials due to their applications in various electronic devices. The benefit of energy storage is that it can reduce the time and plays an important role in energy conservation. Physical applications of storage devices such as Li-ion batteries are much important due to their applications in digital cameras, hybrid electric vehicles, supercapacitors, power sources, portable electronic and recently advanced communication devices[1, 2].Various materials such as carbon-active and redox materials are used as electrode materials[3]. Li-ion batteries have developed an origin of research due to their exceptional physical properties involving better efficiency, enhanced life cycle and easy portability[4]. To develop cost effective, power rated and high storage capacity devices is a matter of high need especially in third world countries. As a part of research, a scope of study have been devoted to develop such kind of electrode materials which are economical with have maximum storage capacity and highest efficiency[5].

Various electrode materials including carbon materials[6, 7], transition metal oxides[8, 9] and hybrid composites are used but due to their inefficient and limited viability, they are not preferred in most of the devices. Carbon materials are less costly but have poor capacitance creating a limitation on their use. Transition metal oxides have been extensively studied to foster

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the storage capacity of Li-ion batteries[10, 11]. The Co_3O_4[12, 13]is mostly preferred among all the other oxides like RuO_2[14], CuO_2[15], NiO_2[16] due to its unique ideal electrode characteristics. It is one of the promising anode materials owing to its low cost, multiple high theoretical capacitance, chemical composition and environmental compatibility. It has potential application in Li-ion batteries, gas sensing and magnetic devices. Ruthenium oxide is toxic and other materials are also limited in their use so we prefer manganese oxide[17, 18], a number of research studies have been done on synthesis of nanostructured Cobalt oxide CO_3O_4 with different experimental techniques such as physical vapor deposition, chemical bath deposition, sputtering[19] and sol-gel methods [20].

Elemental doping of simple metal oxides to form mixed metal oxides has been a way to boost up their electrochemical activities, electronic conductivity and to minimize their cost efficiency. In this case binary systems doping such as Mn-Ni-Co[21] Co-Ni-Cu [22] and Mn-Ni-Cu oxides [23] were also studied. In current work, we study nanostructured Co_3O_4composites with various concentrations of*Al* as an additional dopant. The samples were characterized by X-Ray diffraction (XRD), field emission scanning electron microscope (FESEM), energy dispersive X-ray spectroscopy (EDS), Fourier transformed infrared spectroscopy (FTIR), and cyclic voltametry to explore the different properties of prepared compositions.

The paper is organized as follows. First part presents an introduction to the binary and ternary oxides materials. Second part deals with the experimental procedure.

2. Experimental Method

Al doped Co_3O_4nano structures were synthesized using well established sol-gel based fuel agent assisted self combustion technique. Stoichiometric molar ratios of analytical research grade Aluminium nitrate [Al $(NO_3)_2.9H_2O$], Cobalt nitrate [$Co(NO_3)_2.6H_2O$] were use as the sources of *Al* and Co, respectively. In this preparation Glycine was used as the fuel agent. Calculated molar amounts of reagents for undoped$Co_3O_4$and 0.1 %, 0.3%, 0.5% doped *Al* were weighed on a precise digital balance and subsequently dissolved in 25 ml distilled water. The solution was kept on hot place at 250°C with constant stirring inside a clean fume hood environment. The temperature of gel was raised to 350°C and stirring was subsequently stopped. Fine powder of brownish black color was obtained after intense exothermic combustion reaction. The resulting product was dried and calcinated at 600°C for 4 hours brownish powder was obtained each time. The powder was grinded well using mortar and pestle until fine, homogenous and uniform sized particles were achieved. Structural studies were carried out using X-ray diffraction (XRD) instrument (Bruker D-2 Phaser) operating at 30 kv and 10 ma using Cu K-alpha radiation (λ=1.5406Å) and a step scan size of 0.05°. A field emission scanning electron microscope (FEI Nova 450) was used to observe the morphology of the samples. The microscope was operated at 10 kv and 50k magnification in the secondary electron mode at a distance of 5mm with a through lens detector. Qualitative and quantitative elemental compositions were confirmed using energy dispersive X-ray (EDX) spectrometry (Oxford Instrument Inca X-Act). The measurement of the cyclic voltametry was performed using Gamray Reference 600 potentiostat.

3. Results and Discussions

3.1 X-ray diffraction (XRD) analysis

The X-ray diffraction spectra of undoped and Al doped$Co_3O_4$are shown in Fig. 1. All the XRD patterns are exactly matched with the host pattern containing JCPD card number 01-078-2172.We observe peaks at 2θ values 31.26, 36.77, 44.81, 59.37, 65.20. No other impurity peaks were observed in any pattern. However, peaks are not sharp especially in case of Al incorporated compositions revealing the composite nature of materials. It is clear that there are visible peak shifts to higher angle in the spectrum which is consistent to the previously reported substitutions [30, 31] with lower ionic radii. Crystallite size, cell volume, lattice constant and lattice strain were calculated and observed a significant variation in it with doping of Al content as can be seen in

Fig. 2 and Table 1.Crystallite size and cell volume was observed as 18.79-54.3 nm and 523-527 Å^3, respectively as shown in Table 1. A significant variation in lattice constant (8.06-8.08 Å) and lattice strain (4.36-17.19) was also observed revealed the doping of Al content in to Co_3O_4 structure.

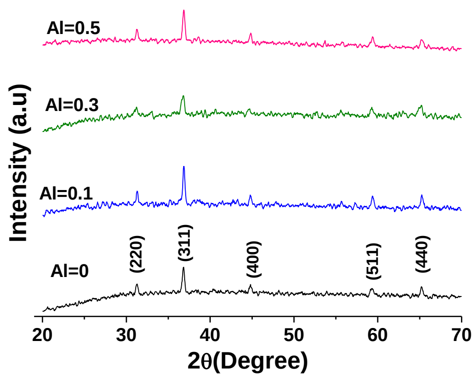

Fig.1 XRD spectra of un-doped and Al incorporatedCo_3O_4 compositions

Table 1. Lattice constant, crystallite size, cell volume, lattice strain and density of compositions

Sample	Lattice Constants A°	Crystallite Size (nm)	Cell Volume (Å^3)	Lattice strain (10^{-3})
UndopedCo_3O_4	8.08±1	53.5±1	527±1	4.36±1
$Al_{0.1}Co_{2.9}O_4$	8.06±1	54.3±1	523±1	9.71±1
$Al_{0.3}Co_{2.7}O_4$	8.07±1	39.74±1	525±1	11.22±1
$Al_{0.5}Co_{2.5}O_4$	8.06±1	18.79±1	523±1	17.19±1

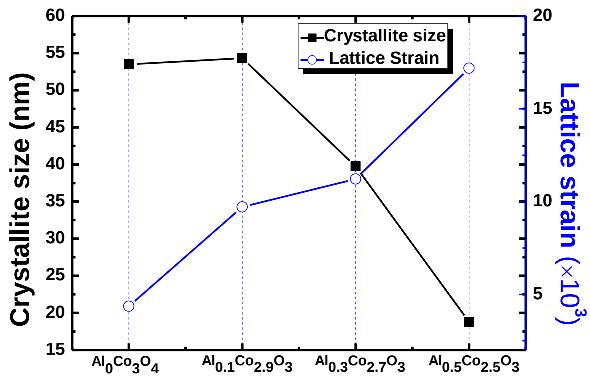

Fig.2. Crystallite size and lattice strain variation with Al content in Co_3O_4

3.2 Field Emission Scanning Electron Microscopy (FESEM)

Morphological studies were carried out using field emission SEM equipped with EDX detector. Fig.3presentthe SEM micrographs of undoped and Al doped Co_3O_4samples. It is visible through images that morphologies are oriented in non-uniform arrangement but they have distinct boundaries and clear shapes like microspheres and fillets with some compact shapes, as well as few cavities in them. Un-doped composition has more ordered morphology with uniform sizes particles. Morphology was disturbed and become more and more disordered with increase in content of Al. Smaller particles can also be observed in Al incorporated compositions which directly related to the very small size of the ionic radii of Al than Co.

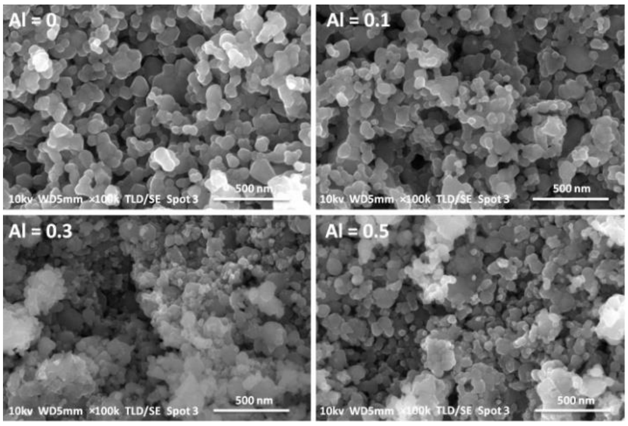

Fig.3SEM micrographs of undoped and Al incorporated Co_3O_4 compositions

3.3 EDX Analysis

Fig. 4 representsthe EDX spectra of all samples. The EDX analysis reveals that Co, O and Al contents are present in approximate stoichiometric ratios in the samples, which ensure the incorporation of Al constituents in the host Co_3O_4structure. Traces of very small carbon content might visible just because of sample remnant. Quantitative EDX analysis is approximately according to the dissolved molar ratio for added elements in all samples as given in table 2. It can be seen that content of Al increased in compositions according to the dissolved reactants.

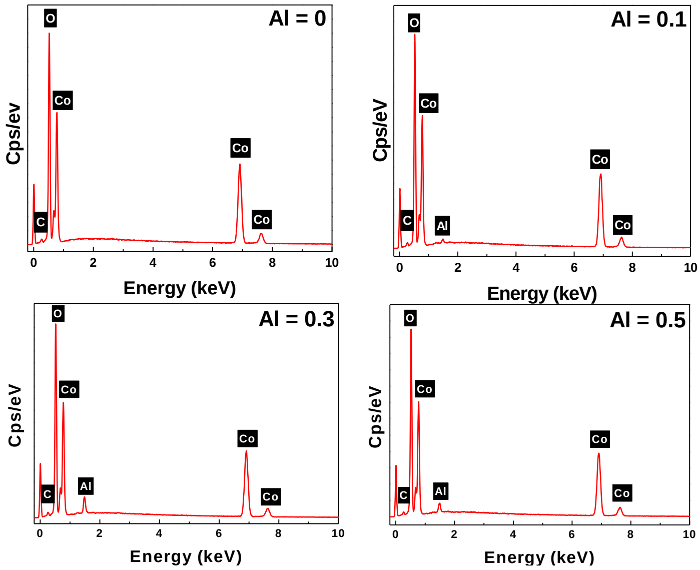

Fig. 4EDX image of undoped and Al incorporated Co_3O_4 compositions

Table 2.EDX elemental compositional measurements

	Undoped		**$Al_{0.1}Co_{2.9}O_3$**		**$Al_{0.3}Co_{2.7}O_3$**		**$Al_{0.5}Co_{2.5}O_3$**	
Element	At. %	Wt. %	At. %	Wt.%	At. %	Wt.%	At.%	Wt.%
O	56.82	28.07	57.69	29.06	48.14	29.56	57.10	29.30
Al	0	0	0.55	0.46	1.52	1.3	2.53	2.19
Co	38.59	70.22	37.00	68.67	36.05	67.51	35.19	66.51
C	4.59	1.70	4.77	1.80	4.29	1.64	5.18	1.99
Total				**100**				

3.4 FTIR Analysis

The FTIR spectra of $AlCO_3O_4$with different concentrations of Al was studied in the range 400-700(cm^{-1}) as shown in Fig. 5.Absorption peaks were observed at 470, 550 and 655 (cm^{-1}).The stretching band at 470 and 550(cm^{-1}) corresponds to the (Co-O) bonds and it validate the presence of CO_3O_4spinel oxides[24-27]. The mode at 655(cm^{-1}) corresponds to vibrational frequency of coordinate O-Co-O bond [28, 29]. The rest of the peaks between 400 to 500(cm^{-1}) show metallic behavior.

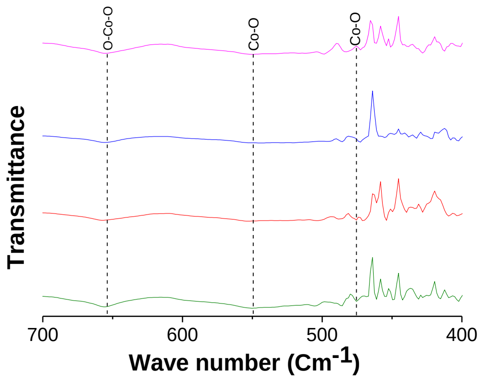

Fig. 5FTIR spectra of $Co_3O_4$with various contents of Al

3.5 Cyclic Voltammetry

It is well understood that shape and structure of materials have direct influence on the electrochemical properties in respect of cyclability and performance [30-33]. However there are few works reported to enhance the electrochemical performance with additional doping in Co_3O_4like materials. The electrochemical performance of all $Al_xCo_{2-x}O_4$ compositions was obtained to determine the Al doping effects. Figs. 6&7show the first cycle curves for charging and discharging process of all samples. Fig. 8 represents the capacity for different composition for various numbers of cycles. It can be observed from the behavior that electrochemical performance was linearly enhanced with addition doping of Al. Much better electrochemical performance was obtained in composition with highest content of Al incorporation.

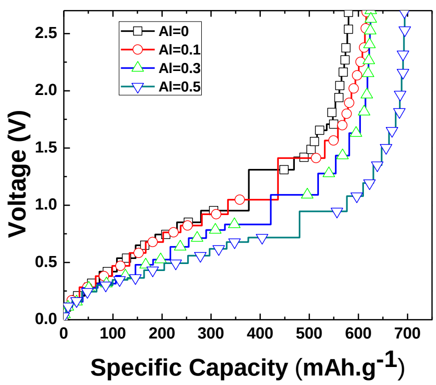

Fig.6First charge curves for undoped and Al incorporated Co_3O_4compositions

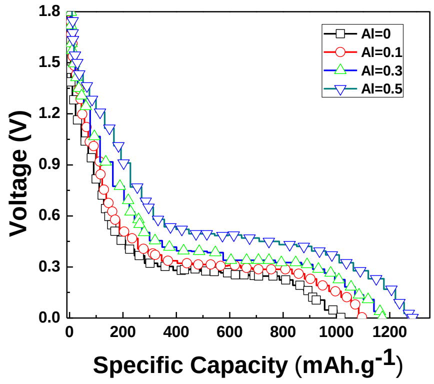

Fig.7First discharge curves for undoped and Al incoporatedCo$_3$O$_4$compositions

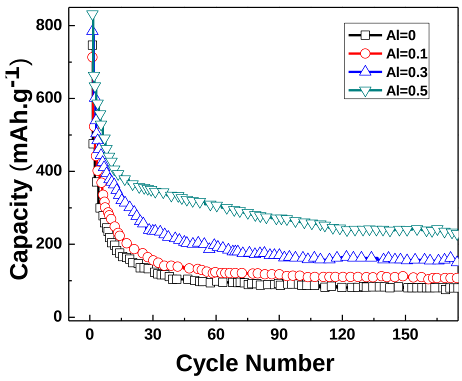

Fig.8 Cyclic performance ofundoped and Al incorporatedCo$_3$O$_4$compositions

4. Conclusions

Al incorporated Co_3O_4 compositions were successfully synthesized with sol-gel based technique. X-ray diffraction analysis confirmed the phase stability of $Co_3O_4$and showing the variation in lattice constant, lattice strain, crystallite size, and cell volume with increase of Al content. FESEM micrographs and elemental compositions were in good accordance with doping trend. FTIR analysis exhibits the *O-Al-O* and *O-Co-O* and *Al-O* bonding and vibrational peaks showing increasing trend with the increase of Al concentration. Enhanced electrochemical performance was observed to significantly enhance with incorporation of Al in host material which is considerably useful for application point of view.

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