Structural and morphological studies of spray pyrolysis derived Mn_3O_4 thin films for supercapacitor applications

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Electrochemical Supercapacitors (ECS), also known as ultracapacitors, are become focus of interest over recent past due to its higher power density and longer cycle life compared to rechargeable batteries and higher energy density compared to conventional electrical double-layer capacitors. To develop an efficient and reliable supercapacitor device, an active electrode material with high storage capacity and reproducible performance is prerequisite [1].

Supercapacitor electrode materials, usually transition metal oxides, have multiple oxidation states, store static electrical energy by reversible faradic surface oxidation-reduction (redox) reactions with electric double-layer storage. RuO_2 shows the promising electrochemical performance at 1.4 V with high specific capacitance of the order of 720 F.g^{-1} . However, it is not yet commercialized due to high cost and toxicity [2]. IrO_2 or CoO_x are other expensive electrodes reported as potential electrodes for electrochemical supercapacitors. On the other hand, cheaper electrode materials based on NiO , Ni(OH)_2 has very low operating potential ($< 0.6 \text{ V}$). Different transition metal oxides, such as, manganese oxide, iron oxide, indium oxide, tin oxide were tested as electrode for electrochemical cell [1]. Among these, Manganese oxide is seen to be promising electrode material for ECS due to its high specific capacitance ($\sim 698 \text{ F.g}^{-1}$), ample availability, low cost, low toxicity and wide range of operating voltage [3].

The energy storage capacity is function of specific capacitance of active electrode materials which is an intrinsic property of the material used and it could be improved by tuning of structural properties of the material by using appropriate synthesis method that provides larger surface area [4]. Therefore selection of materials and synthesis method is an important task.

In this work we have selected Mn_3O_4 as electrode material for electrochemical supercapacitor and it has been synthesized by spray pyrolysis method. Spray pyrolysis is a simple and large area deposition thin film synthesis method. Though this method is bit complicated, fine quality thin films of metal oxide can be obtained at lower temperature. In this study Mn_3O_4 was synthesized using Manganese chloride tetra hydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$: Alfa Aesar 99.9% trace metal basis) metal source for Mn. The

0.2 Molar precursor of Manganese chloride was obtained by dissolving in the DI water. This solution was added in dispenser syringe and sprayed at the rate of 0.1- 0.2cc/min on preheated Stainless Steel (SS) substrate at 300°C . Thickness of the film was varied by changing solution feed rate and microstructure of the film was studied by varying substrate temperature. A continuous brownish colour thin film was obtained. The XRD pattern shown in Figure 1 (a) matches well with JCPDS card no. 00-024-0734 confirms deposited thin film is of Mn_3O_4 with tetragonal crystal structure. The surface morphology of the film is presented in Figure 1 (b) using Scanning Electron Microscope (SEM) image. It is seen from the SEM image that a uniform porous thin film with average grain size of 100nm was obtained. Figure 2 presents LASER surface scan image to confirm uniformity of thin film and roughness. The film thicknesses are varied from 8 to $28 \mu\text{m}$ and surface roughness of the film vary from 0.3 to $3 \mu\text{m}$. A full paper will provide detailed study of different structural and morphological properties on supercapacitance properties of the thin films synthesized by using spray pyrolysis method.

Figure 1: (a) XRD pattern of as deposited Mn_3O_4 thin film (b) SEM image showing surface morphology.

Figure 2: Laser surface scanned image showing surface roughness and uniformity of thin film

References

1. T. Cottineau, M. Toupin, T. Delahaye, T. Brousse, D. Belanger, *Appl. Phys. A*, 82 (2006) pp. 599-606
2. H. Kim, B. N. Popov, *J. Electrochem. Soc.*, 150 (2003) pp. D56-D62
3. D. Dubal, D. Dhawale, R. Salunkhe, V. Fulari, C. Lokhande, *J. All. Comp.* 497 (2010) 166-170
4. Y. Qian, S. Lu, F. Gao, *J. Mater. Sci.*, 46 (2011) pp. 3517-3522