Executive Summary

UGC - Major Research Project (2012-15)
(No: 41-838/2012 (SR) dated 25th July 2012)

Shape and Size-Controlled Synthesis of Co_2AO_4@C (A = Sn, Ti, V and Si) Nanocomposites as an Anodes for Li-ion Batteries

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Introduction

In recent years, the increasing usage of fossil fuels in transport vehicles and the refinery industry has produced more toxic gases such as CO, CO_2, and hydrocarbons, which cause severe health problems in human beings, including pneumonia and the blocking of oxygen from the brain, heart, and other vital organs by CO. Importantly, the continued release of CO_2 increases global warming, leading to severe climate change.[1-3] In order to reduce the emissions of greenhouse gases, the exploitation of green-energy sources, including solar and wind energy, instead of fossil fuels is necessary in the present scenario.

Hence, to reduce air pollution, the peoples are focusing on green-energy sources such as solar and wind energy; they can be considered as important alternative energy sources for sustainable economic growth. However, solar and wind energy, as well as electric cars, require highly efficient energy storage devices. In recent decades, batteries have been viewed as the most promising energy-storage devices, as they can store electrical energy as electrochemical energy. Batteries are classified into two types: primary and secondary batteries. A primary battery is used in its charged state once it converts its chemical energy into electrical energy; it is then discarded as it is not rechargeable. A secondary battery is electrically rechargeable after discharge. To date, the most investigated secondary batteries have been lead-acid, Ni-Cd, Ni–metal hydride, and Li-ion batteries (LIBs).[4] Among these batteries, LIBs have exhibited the best electrochemical performances in terms of long cycle life, low self-discharge, high cell voltage, and no memory effects, and their energy densities are two times and their power densities five times greater than those of current Pd–acid and

Ni-Cd batteries. Hence, LIBs are widely used in different electronic devices, including laptops, mobile phones, and other such electronic devices.[5-7]

In rechargeable batteries, the storage mechanism involves a reversible insertion–extraction of Li ions into and out of the electrode material during the charge-discharge process, based on the rocking-chair concept. While charging (which involves the loss of electrons and Li-ions), Li ions are de-intercalated from the cathode and intercalated into the anode. In the discharge process, Li ions are de-intercalated from the anode and intercalated into the cathode, delivering the energy to an external circuit. This discharge process continues until the potential difference between the two electrodes becomes too small, at which point the cell is fully discharged. Figure 1 depicts a schematic diagram of their function, and the reversible-reaction mechanism of LIBs is described as follows,[8, 9]

Anode: $6C + xLi^+ + xe^- \leftrightarrow Li_xC_6$ (1)

Cathode: $LiCoO_2 \leftrightarrow Li_{1-x}CoO_2 + xLi^+ + xe^-$ (2)

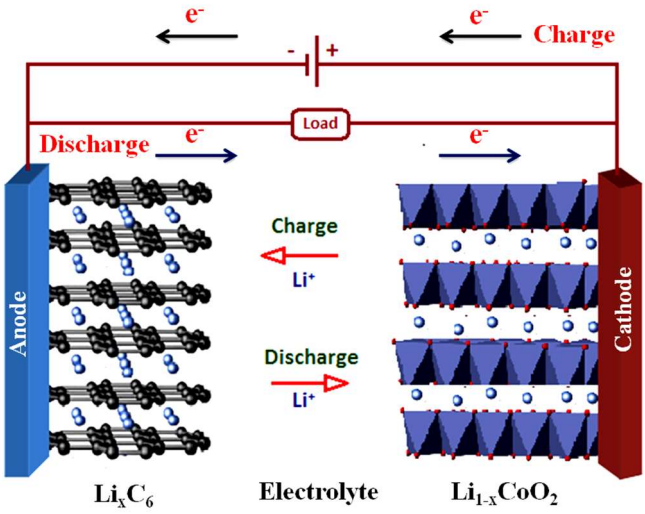

Figure 1. Charge-discharge process of a Li-ion battery (LIB).

Currently, commercially used cathode materials include layer structured $LiCoO_2$ (140–160 mAh g^{-1}); olivine-type $LiFePO_4$ (140–160 mAh g^{-1}); and spinel-type $LiMn_2O_4$ (100–120 mAh g^{-1}), and their practical energy densities versus a graphite anode are 584, 398, and 424 Wh

kg^{-1}, respectively. On the other hand, while using combinations of $Li_4Ti_5O_{12}$ and $LiMn_2O_4$, the obtained energy density is 200 Wh kg^{-1}, which is half of the reported value when using graphite as the anode, since the specific capacity of spinel $Li_4Ti_5O_{12}$ is 175 mAh g^{-1}.[10] The currently used graphite anode has several fascinating properties such as a low working potential versus Li, long cycle life, and low cost. However, its primary drawback is its low reversible capacity, as the diffusion rate of Li is in between 10^{-9} and 10^{-6} cm^2 s^{-1}, resulting in the low power density of this type of battery. Therefore, to further improve the power density of this component, it is mandatory to adopt new strategies and identify novel materials to replace the graphite anode.

Our Proposed Objectives:

- To synthesize the Co_2MO_4 nanostructures (M= Sn, Ti, Si and V) with different shapes and size using the Sonochemical method.
- To make nanocomposites (Co_2MO_4@C) by coating a layer of Carbon on the Co_2SnO_4 nanostructures by Ex-situ methods.
- To characterize the synthesized Co_2MO_4@C Nanocomposites by a various suitable technique such as XRD, FT-IR, Raman spectra, TEM, HRTEM, FESEM.
- To fabricate the 2016 coin cells using the optimized Co_2MO_4@C Nanocomposites as the negative electrode against Li-metal.
- To study the electrochemical performance of the fabricated devices in terms of a) Effect of synthetic methods, b) Influence of size and shape of the nanoparticles, c) Role of carbon composite on Co_2MO_4 nanostructures, and d) Effect in in-situ and Ex-situ methods for making the carbon composites.

Overall Progress of the Project (2012-2015)

In this project report, we have successfully synthesized the A_2BO_4 (A=Co and Zn; B= Sn, Ti, Si, Mn and Ge) compounds, and carbon composite is achieved *in* and *ex-situ* methods. The ultrasonic sonochemistry and polymeric precursor method is adopted for synthesized the Co_2SnO_4 and Co_2TiO_4 compound, respectively, followed by calcination treatment because it requires a high formation temperature. On the other hand, Co_2MnO_4, $Co_{2.85}Si_{0.15}O_4$ solid solution and Co_2GeO_4 compounds are prepared through a simple hydrothermal technique. The prepared samples are characterized by different techniques such as XRD, TGA, FTIR, Raman, FESEM and XPS to identify the phase purity, carbon weight percentage, functional groups, morphological features and composition analysis, respectively. Further, the samples are tested against lithium as a reference using the 2016 coin cell. The summary of the project has given as follows.

- Co_2SnO_4 particles were synthesized by a sonochemical method under different pH conditions, followed by carbon coating through the hydrothermal method. Co_2SnO_4 encapsulated with Carbon was confirmed through the TEM, and HRTEM analysis and the approximate thickness of Carbon was around 20 nm. The cycling stability curve indicates that the pristine-Co_2SnO_4 and Carbon coated Co_2SnO_4 provided a discharge capacity of 777 mAh g^{-1} and 780 mAh g^{-1} at the current density of 40 mA g^{-1} with the capacity retention of 67% and 81%, respectively, in the 20th cycle. The electrochemical study revealed the excellent electrochemical performance of the Carbon coated Co_2SnO_4 particles with superior cycling stability and electronic conductivity.

- $Co_{2.85}Si_{0.15}O_4$ solid solution was successfully synthesized using a facile hydrothermal method for the first time. The structural and morphological features of prepared powders were thoroughly investigated by different techniques. The Rietveld refinement assured the formation of spinel structured $Co_{2.85}Si_{0.15}O_4$ without any impurity phases. The FT-IR and

Raman spectrums revealed the presence of SiO_2 and Carbon with the $Co_{2.85}Si_{0.15}O_4$ solid solution. The X-ray photoelectron spectroscopy inferred that the Co exists in +2 and +3 oxidation state and Si exists in a multivalence state. The surface morphological analysis demonstrated that the formation of cube shape $Co_{2.85}Si_{0.15}O_4$ microparticles is embedded into an amorphous SiO_2 matrix, which was confirmed using the SAED pattern. CV studies confirmed the static nature of amorphous SiO_2 in $Co_{2.85}Si_{0.15}O_4$. Consequently, it was electrochemically active while making composite with Carbon since it reduces SiO_2 into SiOx. The cycling stability of $Co_{2.85}Si_{0.15}O_4$@C composite provided superior electrochemical performance than the pristine $Co_{2.85}Si_{0.15}O_4$. The composite delivers the specific capacity of 444 mAh g^{-1} at 75 mA g^{-1} after 50 cycles with feeble capacity fading. The EIS spectrum corroborates the composite exhibit the lower charge transfer resistance (R_{ct}), and solid electrolyte interphase resistance (R_{SEI}) compared to pristine $Co_{2.85}Si_{0.15}O_4$. The Charge-discharge and EIS studies confirm the carbon composite enhanced the inherent conductive nature and rate capability of pristine $Co_{2.85}Si_{0.15}O_4$ electrode.

- Zinc stannate, Zn_2SnO_4 nanoparticles were successfully synthesized by the facile hydrothermal method. Subsequently, a layer of Carbon was coated on Zn_2SnO_4 nanoparticles by both in-situ and ex-situ methods using glucose as a carbon source. The electrochemical performance of the Zn_2SnO_4@C was examined by dq/dV, charge-discharge, rate capability and electrochemical impedance spectroscopy analysis. Among these, the ex-situ carbon-coated Zn_2SnO_4 showed superior cycling stability, and it delivered the stable specific discharge capacity of 533 mAh g^{-1} at 700 mA g^{-1} over 50 cycles. The EIS analysis indicates that the obtained low charge transfer resistance (R_{ct}) and solid electrolyte interphase (SEI) film resistance (RSEI) of the ex-situ carbon-coated Zn_2SnO_4 controls the SEI film thickness on the outer surface of the active material. Overall, the electrochemical

analysis elucidates that the ex-situ carbon-coated Zn_2SnO_4 shows excellent cycling stability and good electronic conductivity compared with Carbon-free and in-situ Carbon coated Zn_2SnO_4.

- Spinel Co_2TiO_4 was synthesized using the polymeric precursor method and studied as a novel anode material for Li-ion batteries. Carbon coating around the Co_2TiO_4 is achieved through a simple hydrothermal method. The Rietveld refinement studies predict the nominal composition as $Co_{2.05}Ti_{0.95}O_4$ with single-phase cubic spinel structure(*Fd*3*m* space group) in which Co^{2+} ions occupy the tetrahedral 8(*a*) and one-half of octahedral 16(*d*) sites, whereas the other half of octahedral sites is occupied by Ti^{4+} species. Oxygen species are located in the general 32(*e*) sites. The superior electrochemical performance of Co_2TiO_4@C is confirmed by higher initial discharge-charge capacity (1283/418 mAh g^{-1}), high diffusion coefficient (8.70 × 10^{-8} cm^2 $s^{-1/2}$) and lower R_{ct} value (after 50 cycles). This is attributed to the increased electrical conductivity and the creation of new active sites due to the synergistic effect of carbon matrix on Co_2TiO_4, thereby making it a promising candidate for Lithium-ion battery application.
- Overall, the synthesized samples delivered the specific capacity of 533 mAh g^{-1} at 700 mA g^{-1} over 50 cycles for Zn_2SnO_4@C, 742 mAh g^{-1} at 40 mA g^{-1} over 30 cycles for Co_2SnO_4@C, 444 mAh g^{-1} at 75 mA g^{-1} over 50 cycles for $Co_{2.85}Si_{0.15}O_4$@C and 205 mAh g^{-1} at 50 mA g^{-1}over 50 cycles for Co_2TiO_4@C, 622 mAh g^{-1} at 30 mA g^{-1} after ten cycles. The electrochemical performance reveals that the Co_2SnO_4 based anode materials exhibit excellent specific capacity due to their conversion and alloying/de-alloying mechanism. To use this material for the application of LIBs, full cell fabrication with commercially used cathode material and their electrochemical performance are necessary. So we will further construct the full cell using Co_2SnO_4 as an anode and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ as cathode, and their electrochemical performance will be analyzed for real-time Li-ion battery application.

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The outcome of the project

Conferences:

1. Effect of pH on the sonochemical synthesis of Co_2SnO_4 nanoparticles for the application of anodes in Li-ion batteries
   S.Yuvaraj, **R.Kalai Selvan**, C.Sanjeeviraja
   International Conference on Nanoscience and Nanotechnology-2013, held at SRM University, Chennai, March 18-20, 2013.

2. Hydrothermal Synthesis and Characterization of Co_2GeO_4/Rgo@C Ternary Composite As Negative Electrodes for Li-Ion Batteries
   R. Kalai Selvan, S. Yuvaraj, K. Karthikeyan
   ECS Meeting Abstracts, Volume MA2016-03, 180

List of Publications

1. Effect of carbon coating on the electrochemical properties of Co_2SnO_4 for negative electrodes in Li-ion batteries
   S. Yuvaraj, S. Amaresh, Yun Sung Lee and **R. Kalai Selvan**,
   RSC Advances, **2014**, 4, 6407-6416.

2. *In situ* and *Ex-situ* Carbon coated Zn_2SnO_4 nanoparticles as promising negative electrodes for Li-ion batteries
   S. Yuvaraj, W. J. Lee, Chang Woo Lee and **R. Kalai Selvan**
   RSC Advance, **2015**, 5, 67210-67219.

3. Hydrothermal synthesis and characterization of $Co_{2.85}Si_{0.15}O_4$ solid solutions and its carbon composite as ne*gative electr*odes for Li-ion batteries
   S. Yuvaraj, K. Karthikeyan, L. Vasylechko and **R. Kalai Selvan**
   Electrochimica Acta, **2015**, 158, 446-456.

4. Surfactant free hydrothermal synthesis of hierarchically structured spherical $CuBi_2O_4$ as negative electrodes for Li-ion hybrid capacitors
   S. Yuvaraj, K. Karthikeyan, Yun Sung Lee and **R. Kalai Selvan**
   Journal of Colloid and Interface Science, **2016**, 469, 47-56

5. An overview of AB_2O_4- and A_2BO_4-structured negative electrodes for advanced Li-ion batteries
   S. Yuvaraj, **R. Kalai Selvan**, Yun Sung Lee
   RSC Advances, **2016**, 6, 21448-21474

6. Synthesis and electrochemical performances of Co_2TiO_4 and its core-shell structure of Co_2TiO_4@C as negative electrode for Li-ion batteries
   S.Yuvaraj, R.Hari Vignesh, V. Leonid, Yun Sung Lee, **R.Kalai Selvan**
   RSC Advances, **2016,** 6, 69016 – 69026

7. Facile hydrothermal synthesis and characterization of Co_2GeO_4/r-GO@C ternary nanocomposite as negative electrode for Li-ion batteries
   S. Yuvaraj, K. Karthikeyan, **R. Kalai Selvan**
   Journal of Colloid and Interface Science, **2017,** 498, 76-84

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