Graphene doped spray dried ceramic nano oxides for high capacity battery electrodes

Mansi Singh, Poorva Nitin Joshi, Kevin Vattappara, Reghu V R*, Parvati Ramaswamy

Department of Mechanical & Automobile Engineering, CHRIST (Deemed to be University), Bangalore 560 074, India

* Corresponding author: reghu.vr@christuniversity.in

Abstract. Electric vehicles or portable electronic devices have come to rely heavily upon electrochemical devices, such as rechargeable batteries with optimum charge discharge characteristics, current ratings, charge-discharge rate (rate capability), cyclability etc. to perform under the expected service conditions. One of the goals of a rechargeable battery materials researcher is to fabricate materials to realize solid-state batteries with high reliability and lithium–air batteries with ultimate capacities. Most of the materials although possess high theoretical energy density values; invariably suffer from inferior cyclic performance. The performance of these batteries is guided by the electrodes within these devices which in turn depend upon the materials used to fabricate them. Chemical composition and its uniformity, consistency in microstructural features, and adequate choice of various layers that may be in the form of coatings to be overlaid on the base materials mostly comprised of ceramic oxides such as oxides of Li doped with niobates, manganates, vanadate etc. with carbon or graphene coated over layers to provide with the suitable interfacial conductivity as electrode materials in Li-ion batteries. The interfacial layers and the mechanism of interfacial phenomena encompassing the grains play a significant role in determining the performance. Optimum microstructure is obtained by choosing the right processing equipment and spray drying the composition in slurry form provides the most optimum solution. Further, spray drying offers high potential for a transfer from a lab scale technology to industrial level extrapolation. In this paper, nano graphene has been spray dried along with nano alumina grains in water media and polyvinyl alcohol binder to ascertain the free flowability, consistency in formation of graphene over layer on alumina grains as well as uniformity in graphene on alumina composition. The free flowing spray dried graphene coated alumina powders were analysed via SEM, EDS and XRD and results are presented. Additional information based on a review conducted on published information on most popular compositions in terms of electrode materials such as in Li-ion, sodium-ion etc have also been included. In the review section the rapidly increasing literature on spray drying of solutions and suspensions are also included.

1. Introduction

A remarkably high percentage of energy generated worldwide is used up in running industries, maintaining buildings homes and consumed by transportation sector. Our unprecedented dependence on fossil fuel generated energy must be weaned by continuous and systematic research to develop and to increase our capability to enhance the storage capacity of electro-chemical energy. While appearing to be only a long term ‘unbelievable’ goal with many hypothetical possibilities such as to develop extra efficient electrochemical storage devices and integrating the electrical grid with them; this
hypothesis may even become a technological reality if and when a new, high performance, cost effective battery electrode materials are developed.

However, accustomed we may to the low efficiency internal combustion (IC) engines, the world is quite quickly gearing up to welcome the electric vehicles (EV) with superior efficiency. For this technological marvel to be completely accepted by the world in all start of society with varied economy, the major issue arises due to economic and technological challenges. Battery posing the major bottleneck to achieve this technologically marvellous scenario is the battery. The model battery is required to be inexpensive, harmless, with an unprecedented life and energy storage capability. Electrical vehicles including the heavy vehicle categories and simple small rechargeable devices such as wrist watches and calculators: all greatly rely upon the one and only lithium ion rechargeable batteries. Battery electrodes working on principle based on lithium ion intercalation in say graphite anode, involve a variety of materials such as LiCoO$_2$, LiMn$_2$O$_4$, Li$_4$Ti$_5$O$_{12}$ etc. Traditionally used as electrode materials these compositions suffer from the compromised life and recyclability. The limitations are being overcome by incorporating highly conducting carbon and graphene over-layers as composites over the traditional compositions. Newer composition involves composites synthesized via novel processing technologies traditionally used in food technology and pharmaceutical industries e.g. spray drying to fabricate composites with highly favourable characteristics to suit the scientific needs of battery electrode materials. Some of the well-known composites include TiO$_2$-graphene, Co$_3$O$_4$-graphene, SnO$_2$-carbon-graphene, Co(OH)$_2$-graphene, Mn$_3$O$_4$-graphene, Li$_4$Ti$_5$O$_{12}$-carbon-graphene, Fe$_3$O$_4$-graphene, LiFePO$_4$-graphene etc. The carbon and graphene fines over-layers provide the much-needed interfacial phenomenon of conduction between the matrix grains. Spray drying enhances the material characteristics in terms of uniform distribution of the interfacial over-layers, make the composite free flowing for ensuring uniform properties in the electrodes through their free flowability and most importantly provide consistency in properties throughout.

1.1. Review of literature pertaining to spray drying
[1] The experiment focuses on production submicron-sized LiMn$_2$O$_4$ powders by a sol–gel, spray-drying method in which a brown gel precursor was prepared via the reaction of LiOH alkaline solution with 1 M Mn (CH$_3$COO)$_2$. The technique was chosen to be used because of many shortcomings like inhomogeneity, irregular morphology, and the difficulty of controlling the LiMn$_2$O$_4$ material size that were caused by mostly using the standard method of preparation i.e. The (LiMn$_2$O$_4$) powder is usually prepared by a solid-state reaction of lithium salt such as lithium hydroxide, carbonate, or nitrate with manganese compounds such as manganese oxide, hydroxide, or carbonate at a considerably high temperature.

Two of the solutions were taken, 1 M LiOH alkaline and 1 M Mn(CH$_3$COO)$_2$ were prepared to generate the gel precursors. The pH of the alkaline solution was adjusted to 7–8 by adding NH$_4$. Then the alkaline solution was added slowly to the 1 M Mn(CH$_3$COO)$_2$ solutions with intense and constant stirring. After it is done stirring continuously for 2 h until a brown uniform gel precursor formed. The molecular ratio of Lithium: Manganese in the precursor was 1:2. The reagents used were AR grade. The dry precursor powder was produced using spray-dry process using the required equipment. The gel was further sprayed through a rotating sprinkler at the top of a spray-dry vessel, and the gel particles were dried inside this vessel in dry flowing air. The temperature at the entrance of the spray-dry vessel was 260–280°C and the maximum rotating speed of the sprinkler was 50000 rpm. The temperature at the exit for the collecting dry precursor powder was approximately 150°C. Further analysis was done using differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) and also was carried out by Perkin Elmer DTA7 and Perkin Elmer TGA7 analyzers, respectively, to investigate the solid state reaction each working electrode contained 5 mg LiMn$_2$O$_4$ and had a surface area of 0.5 cm$^2$. Both counter and reference electrodes used are lithium sheets. The potentials presented in this paper correspond to the lithium electrode. The charge–discharge curves and the cyclic stability of the LiMn$_2$O$_4$ samples were evaluated in model CR2025 button cells, which consisted of a LiMn$_2$O$_4$-based positive electrode. The amount of LiMn$_2$O$_4$ in the positive electrode was 20 mg. The electrolyte was 1 M LiPF$_6$ was taken in a volume ratio of 1:1 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC).
The results of differential thermal analysis (DTA) and thermogravimetric analysis (TGA) for dry precursor powder in nitrogen atmosphere showed that in the temperature range 50–200°C, the weight loss and the simultaneous temperature decrease can be attributed to the evaporation of adsorbed water. A big weight loss occurs in the temperature range 210–350°C, which reflects the presence of the solid-state reaction that produces spinel LiMn$_2$O$_4$. The further XRD measurement showed that LiMn$_2$O$_4$ samples of pure spinel structure can be produced by heat treatment at comparatively high temperature. The spray-drying method was used to prepare LiMn$_2$O$_4$ powder via DTA, TGA, IR, XRD and SEM analysis, it was shown that the structure and morphology of LiMn$_2$O$_4$ powder were strongly affected by the spray speed and the heat treatment temperature. A sub micro-sized LiMn$_2$O$_4$ powder can be produced using a rotating speed of 15000 rpm and temperature of 700°C. The material has an initial capacity of approximately 128 mAh and good cycling ability in 1 M LiPF$_6$.

[2] Spray dried composites were synthesized by using Li-V oxide with carbon and carbon nanotubes (LVO/C/CNT). The spray dried powders were subjected to calcination in an inert medium to retain the compositional integrity and to avoid oxidation. Glucose was added to ultimately provide Carbon (after calcination) in the matrix and CNT was incorporated in the form of aqueous dispersion in the slurry. The improvement in anode material characteristics were obtained by employing an extremely shallow spray drying strategy to orchestrate Li$_3$VO$_4$/C/CNTs composites with hollow spherical morphology. Electrochemical measurements were carried out by fabricating working electrodes within the coin cells, which were subjected to cyclic voltammetry tests which yielded highly favorable results.

[3] The paper describes spray drying methodology to synthesize nano grained composites with silicon, carbon and Graphene oxide. Two types of anode materials were synthesized (1) nano silicon with sucrose precursor to obtain spray dried sucrose coated nano silicon composite (2) nano silicon and graphene oxide spray dried with sucrose precursor to obtain spray dried sucrose coated nano silicon - graphene oxide composite. The two spray dried powders when calcined at ~800°C in an inert atmosphere (Ar/H$_2$) were reduced to a composite comprised of (1) nano silicon& carbon and (2) nano silicon, carbon and graphene oxide reinforced composite. These two materials were compared with nano silicon as the base electrode material. The role of spray drying in this is experiment is to generate homogenously dispersed constituents described in this section as well as have the potential to develop an industrial scale production. The spray dried powders were characterized for morphology (SEM), chemistry via elemental mapping (EDS), lattice structure by HRTEM, and constituents by TGA. Coin cell electrodes synthesized form the powders were used for electrochemical measurements which included cyclic voltammetry tests. The spray dried composites powders were designated as (a) Si, (b) Si@C and (c) Si@C@RGO. The nanocomposites from C@RGO composite is considered to offer very high cycling stability and better rate capability due to the overlapping conductive layers comprised of carbon covering and wrapped by exceptionally conductive graphene. The Si@C@RGO anode demonstrated superior reversible specific capacity retention. The role of carbon coatings was to reduce the contact zones between the elemental silicon and the electrolyte and enhance the electrical characteristics properties when integrated with graphene. The utility of spray drying approach to synthesize these composites was found to be adequate to scale up to industrial level of production. Undoubtedly, silicon alone and reinforced with carbon and graphene is viewed as the most encouraging possibility for cutting edge anode material. Because of the extraordinary arrangements of carbon coated layers and overlayers of profoundly conducting graphene, the material shows fantastic cyclic soundness with an unrivalled rate capacity. Besides, the composite material anode holds a high reversible explicit limit of 951 mAh/g even at the current density of 2000 mA g$^{-1}$.

[4] The paper is fundamentally used to get the material which is a decent anode material for the better exhibitions. The electrochemical exhibition is yet experiencing low explicit limit and fast limit blurring under huge current, which cannot fulfill the prerequisites of the reasonable application. The generally low capability of Na$^+$ addition/extraction and exceptionally level make Na$_2$Ti$_4$O$_7$ as one of the reasonable Sodium-particle battery anode materials. The connection between the microstructure and electrochemical execution of the Na$_2$Ti$_4$O$_7$ microspheres was deliberately contemplated and determined. As a source of perspective, a customary strong state response routine was applied to orchestrate Na$_2$Ti$_4$O$_7$ powders. The limited availability of Li on the earth’s crust, may lead to the increased raw material coat for Lithium ion batteries (LIB). To overcome the limitations of LIB, researches on sodium – ion battery (SIB) have
on fast track for several years. Its suitability to replace LIB for large scale storage of energy, better availability of sodium compared to lithium and the cost effectiveness attracted the research. Suitable anode materials proposed for SIB include carbon in particle and fiber forms, oxides like V$_2$O$_5$, SnO$_2$, NiCo$_2$O$_4$, Sb$_2$O$_3$, TiO$_2$ nanotubes, and Li$_2$Ti$_5$O$_{12}$. The use of suitable chemicals only cannot improve low specific capacity and rapid capacity fading under large current, which is a challenge to overcome. Use of nanomaterials in the electrodes have shown improvements in performance. The shape of the nano particle assembly also plays an important role in the electro chemical properties and better electrode performance. A microporous structure will help the electrolyte to penetrate the assembly which has large interface area between the electrode and active materials. Though sol-gel reaction is an established method, spray drying process has got some advantages which will avoid the aggregation of nearby nano sized powder particles to form micro spheres.

[5] The paper focuses on the production of cathode material with nano-Sulphur (s) and graphene oxide (GO) composite utilizing spray drying methodology for Lithium Sulphur (Li-S) batteries. The different configurations of the composites synthesized for testing and comparison in this work were (i) GO and (ii) S/GO composites. The constituents were chosen because Sulphur has high theoretical capacity and it is widely available and low-cost, while Graphene Oxide (which was doped with Nitrogen), with functional groups of O, that could inhibit reactions and products formed from sulphide reactions, to interfere in the battery operation. The suspension for spray drying was produced by adding nano-S suspension (prepared for commercial powders) dropwise into a continuously stirred GO solution (prepared by Hummers method). After the spray drying process, the composite was completely dried. The powder after the spray drying process, was characterized with XRD (crystal structure), SEM and TEM (morphology), TGA (the amount of each constituent in the composite) and EDS (elemental mapping). Other characterization techniques used were Raman spectroscopy and FT-IR spectrometer (to check for formation of functional groups in GO). The powders were added to other binders and conducting medium to make working electrode in 2025-type coin cells. The cells were then subjected to various electrochemical tests such as cyclic voltammetry, galvanostatic and impedance studies. The XRD pattern for S/GO composite, with reduced intensity peaks for S, indicated the enveloping of S particles in the composite powders. The TGA analysis revealed the amount of S in the composite to be close to 60% (~58%). The Electron Microscope images show homogenous and spherical morphology, which could improve the electrical conductivity and cycling performance for the cathode material in Li-S battery. The paper investigates the utilization of spray drying technique for electrode fabrication in Li-S batteries, which gives excellent performance numbers in various metrics of discharge capacity and cycling performance. The role of spray drying in this is experiment is to generate homogeneously dispersed constituents.

[6] The paper mainly focuses on testing and investigating the structural and electrochemical properties of Li$_x$V$_2$(PO$_4$)$_3$ doped with Fe and Al by spray drying with the help of carbo-thermal solid-state reaction. The properties were investigated and the diffraagrams and micrographs obtained by XRD, SEM and galvanostatic charge/discharge studies. Following carbothermal reduction, the electrode material was synthesized via spray drying. The detailed process methodology is as follows. Stoichiometric mixture of LiOH.H$_2$O, NH$_4$VO$_3$ and NH$_4$PO was first dissolved in water (200ml) and was uniformly stirred at the speed of 300rpm maintaining temperature of 80°C, then citric acid with acted as a chelating agent with a reductive agent was added to the solution under magnetic stirring at 120°C for 1 hour, PH of the solution was maintained at 9 and 12 so that the mixture was homogenous. The obtained solution was then spray dried at 10ml/min maintaining inlet and outlet temperature as 220°C and 110°C, the solution was then preheated at 300°C for 5h, the resulting pellets were then kept in argon atmosphere for 10 h at 700°C and then cooled to room temperature. The procedure which was carried out for Al and Fe doped LiPO were same expect the stoichiometric ratio in which Al (NO$_3$)$_3$ and FeC$_2$O$_4$.2H$_2$O were used. The crystalline Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ solid-state electrolyte was processed using stoichiometric ratios of Li$_2$CO$_3$, GeO$_2$, NH$_4$H$_2$PO$_4$, and Al$_2$O$_3$ the mixture was heated twice first at 500°C for 2h and ground and then at 800°C for 6 h and was then further sintered for 2h at 900°C.

[7] The paper focuses on the production of composites with nano-Silicon monoxide (SiO), Carbon nanofibers (CNF) and graphene utilizing the facile/non-complex spray drying methodology with pyrolysis. The different configurations of the composites synthesized for testing and comparison in
this work were (i) nano-SiO (ii) SiO@CNF and (iii) SiO@CNF&G composites. The constituents are selected for the different roles fulfilled by them such as SiO is the main electrically-active component (Si has very high theoretical capacity), CNF are interlinked to form the matrix to provide stability for the Si and provide pathways for the liquid electrolyte in the cell to interact with SiO and finally graphite to improve the electrical conductivity. The colloid for spray drying consisted of both raw materials, solvent, and binder. The raw materials such as SiO (ball milled from bulk-SiO to nano size), CNF and graphite (milled to smaller size), deionized water (solvent for SiO) and citric acid (organic binder). The spray dried precursor was pyrolyzed at 900°C in N₂ atmosphere. The powder after the spray drying process, was characterized with XRD (phase components), SEM and TEM (morphology) and EDS (elemental mapping). The powders were ground to make half coin cells. In the cell, the working electrode consist of the active composite and other binders, which were then subjected to various electrochemical tests such as cyclic voltammetry and impedance studies. The XRD characterization showed pattern for SiO, SiO@CNF and SiO@CNF&G composites, with expected peaks for elemental Si (due to SiO growing in size during pyrolysis) and C (due to addition of CNF and graphite) in SiO@CNF and SiO@CNF&G composites. The Electron Microscope images show spherical morphology, with CNF seen to be effectively forming a network to accommodate Si and G while providing pathways for electrical conductivity. Because of the interconnected structure of CNF and the enhanced conduction due to graphene, the material shows fantastic reversibility, initial coulombic efficiency. Besides, the composite material anode holds a high reversible explicit limit of ~583 mAh/g. The role of spray drying in this experiment is to show the ease in producing silicon-based anodes compared to other methods as well as have the capability to build an industrial scale production.

1.2. Scope of work

This paper focuses on presenting a typical case involving spray drying nano ceramic powders with graphene to ensure uniformity in the composite formation and consistency in the graphene over-layer. The finding may be extrapolated to many other ceramic oxides that may offer huge potential to serve as battery electrodes provided the merit of spray drying the ceramic with graphene is confirmed, a goal which has been achieved in this work.

2. Experimental work

2.1. Composite fabrication

The raw materials for the fabrication of the Al₂O₃/Graphene composite, were commercially available - nano-Alumina ceramic powder and graphene powder, with polyvinyl alcohol (PVA) used as binder and distilled water used as the solvent. The preparation of the slurry started with the mixing of the binder and solvent with stirring equipment with the raw materials being added slowly into the slurry[8]. The slurry preparation and spray drying process parameters were optimized after several runs, the details of which are given in the table 1 below. The spray drier used in this work was SPD-P-111 by Technosearch instruments, India.

| Trial no | Distilled water (ml) | PVA (g) | Raw material (g) | Output (g) Chamber | Output (g) Cyclone | Yield% | Remarks      |
|----------|----------------------|---------|-----------------|--------------------|--------------------|--------|--------------|
| 1        | 220                  | 1.3     | 20              | 4.4                | 8.67               | 22     | Process completed |
| 2        | 300                  | 1.8     | 30              | 7.24               | 13.45              | 24.13  | Process completed |
| 3        | 300                  | 1.8     | 30              | 3.1                | 3.11               | 10.33  | Nozzle clogged  |
| 4        | 200                  | 1.8     | 20              | 11.16              | 3.78               | 55.8   | Process completed |

Table 1. Optimization Trials Of Spray Drying Parameters And Compositions Of Binder, Distilled Water, Pva And Raw Materials
Based on the optimization trials conducted, the spray dried powder from Trial no. 4 was selected for further characterizations. The lab scale spray drier used for the experimental work is shown in Figure 1 and the collecting area for the spray dried powder within the chamber is shown in Figure 2.

Figure 1. Spray Drier SPD P-111

Figure 2. Collecting area for the spray dried powder.

2.2. Material Characteristics

After synthesis, the spray dried powders were characterized, for checking the dispersed phase composition in the powder with XRD (XPERT 3 system with Cu anode, Kα radiation, \( \lambda = 0.15406 \, \text{nm} \)), the morphology of the powders by Scanning Electron Microscope (SEM) and the uniformity of the elemental distribution in the powders using Energy dispersive spectroscopy (EDS). Figure 3 shows the starting materials, graphene is shown in Figure 3(a), Nano sized alumina in Figure 3(b) and spray dried product is shown in Figure 3(c).

Figure 3. Photograph of (a) Graphene (b) Nano alumina (c) Spray dried Graphene-Alumina.
3. Results and Analysis

3.1. XRD pattern for phase composition
As already brought out in literature and the experimental work, presence of the element providing the electrical conductivity is of paramount importance in the synthesis of battery electrode materials. The X-ray diffractogram depicting the presence of small quantity (0.5 %). The indexing parameters for the composite are shown below in table 2.

Table 2. Indexing parameters in the identification of the compounds present in the powders.

| Visible | Ref. Code   | Score | Compound Name | Displacement [2θ.] | Scale Factor | Chemical Formula |
|---------|-------------|-------|---------------|--------------------|--------------|------------------|
| *       | 98-005-2024 | 90    | Corundum      | 0.000              | 0.820        | Al₂O₃            |
| *       | 98-007-6767 | 22    | Graphite 2H   | 0.000              | 0.024        | C1               |

Figure 4 shows the XRD pattern to confirm the presence of both alumina and graphene in the spray dried powder. The pattern gives a good indication of the uniformity in the powders, without any formations of unexpected peaks for other compounds.

Figure 4. XRD pattern to confirm the presence of alumina and graphene (C).

The sharp peaks gave clear indication of crystalline pattern and absence of any unidentified peaks in the pattern confirmed the absence of any impurities in the composition.

3.2. SEM and EDS images for morphology and elemental analysis
Figures 5 & 6 show the SEM micrographs for the morphology of the dispersion media. Both the figures show the uniform dispersion of graphene in nano alumina matrix, which was later confirmed by EDS.
Figure 5. SEM image of the dispersion media.  

Figure 6. Enlarged view of the dispersion.  

Figure 7 shows the dimensional and morphological details of the spray dried nano-alumina-graphene composite.  

Figure 7. Spray dried nano alumina and graphene composite.  

The advantages of the spray drying over mechanical mixing is the homogeneity throughout the material. To confirm this, EDS analysis was conducted at 4 different portions. Figure 8 (a) shows the area selected for analysis and Figure 8 (b) shows the EDS pattern and the chemical composition at the inspected area. Similarly Figure 9 (a) and (b) shows another area from the spray dried alumina-graphene and the EDS pattern and the element analysis, respectively. Figure 10 (a) & (b) and Figure 11 (a) & (b) depicts 2 other areas selected from the bulk of the powder and the EDS pattern and chemical analysis. The EDS analysis reveals almost uniform composition at all regions which is as per
the expected result from the spray drying. Based on the XRD pattern and the SEM morphology images, the spray drying process parameters selected in this study, would be useful for future experiments on other electrode materials compositions.

![Figure 8](image1.png)

**Figure 8.** (a) Selected area (a1) for EDS analysis (b) EDS spectrum and element analysis at area(a1).

![Figure 9](image2.png)

**Figure 9.** (a) Selected area (a2) for EDS analysis (b) EDS spectrum and element analysis at area(a2).

![Figure 10](image3.png)

**Figure 10.** (a) Selected area (a3) for EDS analysis (b) EDS spectrum and element analysis at area(a3).
Figure 11. (a) Selected area (a4) for EDS analysis (b) EDS spectrum and element analysis at area (a4).

4. Conclusions

The research into the application of spray drying method in synthesizing battery electrode materials has gathered some momentum in recent years. This is evident from review of the work done by different research groups in this paper, which were looking into the fabrication of both cathode and anode from different novel composites. There is need for alternate material composites for Li batteries to improve on their energy outputs and elements which are inexpensive and abundant in nature to replace some of the currently used expensive raw materials. The advantages for utilizing spray-drying method are manifold which include homogenous distribution of components in the composite material matrix, consistent powder characteristics and the ability to easily alter the properties according to different specifications. In many of the works reviewed here, even though spray-drying was done at a laboratory-scale, but the intension was to scale-up the production to the next level in terms of industrial production quantities with maximum reproducibility. The experimental work done in this paper is an attempt at reproducing the homogenous distribution of graphene in alumina. The results from the work confirms the homogenous distribution and control on the particle size distribution using spray drying method. Although further work is required, in terms of iterative experiments and optimizations of parameters, for effective utilization of spray drying process.

5. References

[1] Wan C, Nuli Y, Wu Q, Yan M and Jiang Z 2003 Journal of applied electrochemistry 33 107-12
[2] Yang Y, Li J, Chen D and Zhao J 2016 Journal of The Electrochemical Society 164 A6001
[3] Pan Q, Zuo P, Lou S, Mu T, Du C, Cheng X, Ma Y, Gao Y and Yin G 2017 Journal of Alloys and Compounds 723 434-40
[4] Zou W, Li J, Deng Q, Xue J, Dai X, Zhou A and Li J 2014 Solid State Ionics 262 192-6
[5] Tian Y, Sun Z, Zhang Y, Wang X, Bakenov Z and Yin F 2018 Nanomaterials 8 50
[6] Kee Y, Dimov N, Kobayashi E, Kitajou A and Okada S 2015 Solid State Ionics 272 138-43
[7] Hou X, Wang J, Zhang M, Liu X, Shao Z, Li W and Hu S 2014 RSC advances 4 34615-22
[8] Gowtham Sanjai S, Anathakrishna B, Sai Sumanth M, Srideep S and Ramaswamy P 2019 Materials Today: Proceedings 19 708-14

Acknowledgments

The authors gratefully acknowledge the support provided to perform the experiments and the permission given by the management of CHRIST (Deemed to be University) to publish this paper.