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PAGES: 47-51

ORIGINAL PDF URL: http://www.epstem.net/tr/download/article-file/2233995



The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM), 2021

Volume 16, Pages 47-51

IConTES 2021: International Conference on Technology, Engineering and Science

Synthesis of $rGO/g-C_3N_4$ Composite Cathodes for Li – Ion – Oxygen Battery

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Abstract: The low-cost electro-catalysts are very crucial for the lithium-ion oxygen battery electrodes. In this work porous reduced graphene oxide (rGO) was synthesized by the chemical methods and mixed with melamine to obtain rGO/graphitic- C_3N_4 (g- C_3N_4) composite which compose of 50% rGO and 50% g- C_3N_4 . SEM, XRD and FTIR characterizations showed that the synthesized composite structure reflected most of the features of the rGO structure. The synthesized rGO/g- C_3N_4 composite was prepared as the cathode for the Li-ion-oxygen battery and its discharge/charge performance was determined. The composite cathode demonstrated a distinctive performance since g- C_3N_4 catalyzed both the oxygen reduction and oxygen evolution reactions during the discharging and charging. This work showed that rGO/g- C_3N_4 composite electrode was quite promising as the cost-effective cathode for the Li-ion-oxygen batteries.

Keywords: Lithium oxygen battery, Reduced graphene oxide, g-C₃N₄

Introduction

The lithium (Li) ion oxygen batteries have higher energy density $(2 - 3 \text{ kW kg}^{-1})$ than any other known batteries. The discharging and charging processes in the Li ion oxygen batteries involve oxygen reduction and oxygen evolutions reactions, respectively (Bruce et al., 2012). Therefore, the performances of the Li ion oxygen batteries are directly controlled by the porosity level and the loaded electro-catalysts of the cathode. The electro-catalysts are expected to have high stability, low cost and high efficiency. The most widely used electro-catalysts are carbon materials (Zhang et al., 2013), precious metals (Jung et al., 2013) and transition metal oxides (Han et al., 2014).

Graphitic carbon nitride $(g-C_3N_4)$ can be simply synthesized from a convenient precursor via series of polycondensation reactions and it can be used as electro-catalyst for the Li ion oxygen battery cathodes since it catalyzes both the oxygen reduction and oxygen evolution reactions (Niu et al., 2012). In this work $g-C_3N_4$ was chemically mixed with the porous reduced graphene oxide (rGO) to get efficient composite cathode for the Li ion oxygen battery. In the composite electrode, while $g-C_3N_4$ was expected to catalyze oxygen reactions, porous rGO provided large and highly conductive surface areas to the cathode.

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Method

The mixture of acids, H_2SO_4 : H_3PO_4 (360:40 mL), was slowly added into a mixture of KMnO₄ (18.0 g) and graphite flakes (3.0 g) to synthesize graphene oxide (GO). Then the reaction mixture was heated to 50°C and stirred at 300 rpm for 12 h. The reaction mixture was cooled down to RT normally and poured onto ice (400 mL) and at the same time H_2O_2 (3 mL) was added drop wise to the mixture. After this step, the mixture was filtered and washed. The initial washing step was performed with 30% HCl solution and this step was repeated as necessary until the supernatant becomes transparent. Then the washing process was continued with DI water and ethanol until achieving a neutral pH value. All the washing process was performed by the centrifugation at 6000 rpm for 30 min. The resulting solid was dispersed in DI water by ultrasonication at a concentration of 1.0 mg ml⁻¹.

Silica (SiO₂) nanoparticles were synthesized on the basis of hydrolysis of tetraethyl orthosilicate (TEOS) in pure water/ethanol medium in which ammonia acts as a catalyst. The range of 0.5 - 3 M for NH₃ and 0.1 - 0.5 M for TEOS was used. Pure water, ammonium hydroxide and ethanol were mixed at 50°C for 5 min. Then, TEOS was added to the mixture and stirred for 6 h, and then the mixture was centrifuged in isopropyl alcohol (5000 rpm, 30 minutes). At the end of the washing process, the final solid content was left to dry at 80°C under vacuum. The synthesized silica nanoparticles were dispersed in pure water with the help of sonication. Then, HCl, methyl group containing (-CH₃) Pluronic F108 and dimethoxydimethylsilane were added to the prepared silica solution and they were mixed for 24 h. Then the final suspension was brought to a neutral pH with the help of NH₄OH. The prepared GO suspension was mixed with the neutralized suspension for 24 h at RT, then the solid content of the obtained suspension was centrifuged at 6000 rpm for 1 h and then it was dried in a vacuum controlled atmosphere at RT.

For the synthesis of porous rGO, the synthesized GO/SiO_2 nanostructures were first heat treated at 900°C for 5 h in Ar atmosphere. Then, silica nanoparticles were etched with sodium hydroxide and then they kept in an Ar atmosphere at 900°C for 5 h. In order to prepare porous rGO/g-C₃N₄ composite, porous rGO was mixed with melamine in ethylene at 60°C and then mixture was stirred until getting dried solid structure. The solid mixture was then putted into sealed alumina crucible and it was heated up to 550°C at a rate of 3°C min⁻¹ and kept at 550°C for 3 h under Ar atmosphere. After air cooling in Ar atmosphere, the rGO/g-C₃N₄ composite was obtained. The composition of mixture was arranged so that the final composite composed of 50% rGO and 50% g-C₃N₄ by weight.

The metallic lithium was used as the counter electrode in the battery cell. The cathodes were prepared by mixing composite and poly (vinylidene fluoride) (PVDF) (80:20 wt%) in the 1-methyl-2-pyrrolidone (NMP). Then the slurry was coated onto the gas diffusion layer (TGP-H-060). Before the battery assembly, the electrodes were dried in a vacuum oven at 100°C for overnight. An electrolyte solution of 1 M LiTFSI in DME solvent was used at all the discharge/charge tests conducted in this study. The air battery cell (EQ-STC-LI-AIR, MTI Corporation) was assembled in a glove box (H₂O and O₂ \leq 0.1 ppm) and it tested galvanostatically by using Gamry Reference 3000 Potentiostat/Galvanostat/ZRA. The measurements were conducted in a dry pure oxygen atmosphere (1 atm). The mass loading of the cathode was about 0.5 mg cm⁻². The discharge and charge current density was used as 0.05 mA cm⁻² (100 mA g⁻¹ composite cathode).

X-ray diffraction (XRD) analyses were performed on a PANalytical Empyrean diffractometer with Cu K-alpha radiation at a scanning rate of 2° min⁻¹. The morphologies of the electrodes were examined with a ZEISS Ultraplus scanning electron microscope (SEM). FT-IR spectra was obtained using a PerkinElmer Spectrum Two.

Results and Discussion

Characterizations

Micrographs of $g-C_3N_4$ and porous rGO are provided in Figures 1a and 1b. The large particular appearance of $g-C_3N_4$ and the porous nature of rGO are observable clearly in the figures. The morphology of the 50% rGO and 50% $g-C_3N_4$ composite in Figure 1c is very similar to that porous rGO in Figure 1b since the expected density of the porous rGO is much lower than that of $g-C_3N_4$ and therefore, the volume percentage of the porous rGO rather than that of $g-C_3N_4$ in Figure 2 where rGO shows a graphitic peak at at $2\theta = 26.2^{\circ}$ (with an interlayer spacing of 0.34nm, indicating the existence of graphene atomic layers) and $g-C_3N_4$ shows one weak peak at $2\theta = 13.1^{\circ}$

((100) crystal face indicating the interplanar distance between the nitride pores) and strong peak at $2\theta = 27.4^{\circ}$ (the characteristic feature of the (002) crystal face indicating the interlayer stacking of the conjugated aromatic systems).



Figure 1. Micrographs of (a) g-C₃N₄ (b) porous rGO and (c) composite.



Figure 2. Comparison of the XRD patterns of g-C₃N₄, porous rGO and the composite.

The FT-IR spectra of $g-C_3N_4$, porous rGO and the composite are compared in Figure 3. The large absorption peak of $g-C_3N_4$ in a 3000 – 3200 cm⁻¹ range belongs to the stretching vibration modes of N-H bonds and those at 1230, 1305, 1370, 1550 ve 1630 cm⁻¹ belong to CN hetero-cyclic stretching vibration modes. The peak at 1705 cm⁻¹ belongs to the stretching vibrations of C=O and that at 1595 cm⁻¹ to the vibrations of sp2 hybrid C-C for rGO in Figure 3. Once again, the FT-IR spectra of the composite reflects most of the features of that of rGO.



Figure 3. Comparison of the FT-IR spectra of g-C₃N₄, porous rGO and the composite.

Discharge - Charge Tests

The discharge - charge curves of the Li-ion oxygen battery contains rGO and composite cathodes are shown in Figures 4a and 4b, respectively, up to the 50^{th} cycle. The discharge capacities depend on the discharge - charge

cycle number are provided in Figure 4c for both cathodes. Obviously despite the structural similarities of the composite to the rGO (in Figures 1, 2 and 3), it has much better electrode performance with respect to the rGO. The catalytic action of the $g-C_3N_4$ on the porous rGO surface towards both the oxygen reduction and evolution reactions are clearly observed in this work.



Figure 4. Discharge – charge curves of Li-ion oxygen battery contain (a) porous rGO and (b) composite cathodes, and (c) comparison of the discharge capacities depend on the cyclic number.

Conclusion

The porous reduced graphene oxide (rGO) - graphitic- C_3N_4 (g- C_3N_4) composite consisted of 50% rGO and 50% g- C_3N_4 was synthesized. SEM, XRD and FTIR characterizations showed that the synthesized composite structure reflected most of the features of the rGO structure. The composite had much better cathode performance as compared to the cathode performance of the porous rGO in the Li-ion-oxygen battery.

Acknowledgements

This work was supported by The Scientific and Technological Research Council of Turkey under the contract number 219M269.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

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To cite this article:

Lokcu, E., Kacar, N., Ozden, R.C., & Anik, M. (2021). Synthesis of rGO/g-C3N4 composite cathodes for Liion – oxygen battery. *The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM), 16*, 47-51.