



Short communication

One-pot, glycine-assisted combustion synthesis and characterization of nanoporous LiFePO₄/C composite cathodes for lithium-ion batteriesN. Kalaiselvi¹, A. Manthiram*

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ABSTRACT

Nanoporous LiFePO₄/C composite cathodes have been synthesized by a novel one-pot, glycine-assisted combustion (GAC) method in presence of 2 wt.% Super P carbon in both Ar and 90% Ar–10% H₂ atmospheres at 750 °C for a short time of 6 h. While the Ar atmosphere offers phase pure samples, the Ar–H₂ atmosphere leads to the formation of impurity phases as indicated by X-ray diffraction data. The combustion-initiated expulsion of gases aids the formation of a nanoporous LiFePO₄/C composite structure as evident from electron microscopic analysis, which could allow easy penetration of the electrolyte and realization of an electronic–ionic 3D network. The nanoporous LiFePO₄/C sample synthesized in Ar atmosphere exhibits a high discharge capacity of 160 mAh g⁻¹ with 3% capacity fade in 50 cycles and high rate capability. With a short reaction time, the GAC method offers an energy efficient approach to synthesize high performance olivine LiFePO₄/C composite cathodes.

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1. Introduction

Olivine LiFePO₄ has emerged as one of the leading cathode candidates for high power lithium-ion cells as the covalently bonded PO₄ groups offer excellent thermal stability while Fe is inexpensive and environmentally benign. The main drawback with LiFePO₄ is the low electronic and lithium-ion conductivities. To overcome this problem, reduction in particle size as well as cationic doping or coating with conductive carbon have been pursued [1–6]. These strategies have improved the electrochemical performances significantly. Further gain in performance could be achieved by having a nano-network composed of mesopores that are filled with electrolyte and electronically conducting agents like carbon. For example, even the highly insulating silicates have been shown to exhibit remarkable electrochemical activity by nanostructuring [7]. Similarly, the combination of nanostructuring with highly conductive agents has been shown to enhance the cycling behavior of LiFePO₄ [8–10]. With this perspective, we focus here on the synthesis of nanoporous LiFePO₄/C composite cathodes.

Formation of porous nanostructures has been reported by employing sol–gel and co-precipitation synthesis approaches [11–14]. Quite different from the reported approaches [15], the

present study explores a first systematic study on a fuel-initiated, glycine-assisted combustion (GAC) synthesis method, in which simultaneous firing of the added Super P carbon along with the combustible precursor mix is performed in order to have a good wrapping or coating of carbon over LiFePO₄ surface. Such a combination of precursor mix on heating in Ar or 90% Ar–10% H₂ atmosphere could result in the formation of nanoporous LiFePO₄/C composite, in which the evolving gases from the combustible fuel are believed to penetrate through the fluffy mass to form the nanoporous ultrafine powder. In this method, the added carbon can get distributed uniformly throughout the porous surface of each particles of LiFePO₄ as the carbon is added to the initial solution precursor. While the carbon coating can overcome the electronic conductivity limitations, the pores that are formed due to the escape of gases from the combustible fuel can enhance the ionic conductivity via an easy percolation of the electrolyte. Thus, this GAC method provides the possibility of formation of a mixed electronic–ionic conducting 3D network holding LiFePO₄/C.

Compared to the various synthesis approaches reported for LiFePO₄ such as mechanical alloying [16,17], sol–gel [18,19], co-precipitation [20], microwave process [21], hydrothermal [22,23], emulsion drying synthesis [24,25], carbothermal reduction [26], vapor deposition [27], spray solution technology [28], and chemical lithiation of FePO₄ [29], the present GAC synthesis approach with carbon incorporation could provide some advantages. In addition to being a one-pot synthesis approach [30] to obtain carbon-coated LiFePO₄, the unique nanoporous microstructure formed with carbon coating can provide easy access to the electrolyte, enhancing

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the rate capability. It involves a much lower carbon content of 2 wt.%, and the presence of carbon in the initial reaction mixture can prevent the oxidation of Fe^{2+} to Fe^{3+} during the synthesis process [31–34]. The one-pot synthesis of nanoporous LiFePO_4/C composite cathodes by the GAC approach and the characterization of the products are presented here.

2. Experimental

Stoichiometric amount of lithium nitrate (Across Organics), iron oxalate (Alfa Easer), and ammonium dihydrogen phosphate (Across Organics) were dissolved in minimum quantity of deionized water and heated with stirring on a hot plate to get a homogenous solution. A solution obtained by dissolving glycine (Across Organics) in minimum amount of water was then added to this hot solution and stirred further to get a clear solution. The LiFePO_4 :glycine molar ratio in the reaction mixture was 1:2. A minimum amount of 2 wt.% Super P carbon was added to the hot solution and the process of heating and stirring on the hot plate was continued until a fluffy mass was formed. The foamy product thus obtained was collected and heated in a furnace at 300°C for 12 h, followed by a high temperature heating at 750°C for 6 h in flowing Ar or 90% Ar–10% H_2 atmosphere. The ultrafine powders thus obtained were then subjected to physical and electrochemical characterization.

X-ray diffraction (XRD) patterns were recorded on a Philips diffractometer with $\text{Cu-K}\alpha$ radiation, scanning electron microscopy (SEM) images were recorded with a JEOL JSM-5610 SEM, and transmission electron microscopy (TEM) data were collected with a JEOL 2010F TEM operating at 200 keV. Raman spectra were recorded from a Renishaw Raman Spectrometer. Electrochemical charge–discharge measurements along with cyclability and rate capability data were collected with CR2032 coin cells as reported elsewhere [35]. The coin cells were fabricated with the LiFePO_4/C composite cathode, metallic lithium anode, 1 M LiPF_6 in 1:1 diethyl carbonate/ethylene carbonate electrolyte, and Celgard polypropylene separator. The cathodes were prepared by mixing 75 wt.% active materials with 20 wt.% conductive carbon and 5 wt.% polytetrafluoroethylene (PTFE) binder, rolling the mixture into thin sheets, and cutting into circular electrodes of 0.64 cm^2 area.

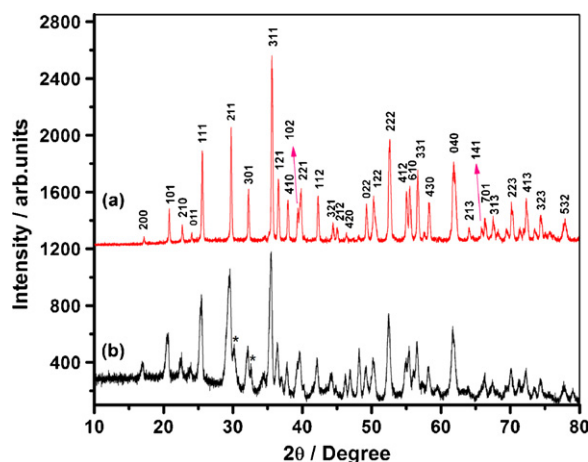


Fig. 1. XRD patterns of the LiFePO_4/C composites synthesized in (a) Ar atmosphere and (b) 90% Ar–10% H_2 atmosphere. The reflections marked with * refer to impurity phases.

3. Results and discussion

3.1. XRD analysis

Fig. 1 depicts the XRD patterns of LiFePO_4/C synthesized in Ar and Ar– H_2 atmospheres. While the sample synthesized in Ar atmosphere could be indexed on the basis of the orthorhombic $Pnma$ space group without any impurity phases (**Fig. 1a**), that synthesized in Ar + H_2 atmosphere shows trace amounts of impurity phases like $\gamma\text{-Fe}_2\text{O}_3$ and magnetite Fe_3O_4 (**Fig. 1b**). Least square fitting of the XRD data gave the lattice parameter values of $a=10.33$, $b=6.01$, $c=4.69$ for the sample synthesized in Ar atmosphere and $a=10.32$, $b=6.02$, $c=4.696$ for the sample synthesized in Ar– H_2 atmosphere. The average grain size calculated from the Scherrer equation was found to be around 20–38 nm for both the samples. The data reveal that the GAC method is capable of offering phase pure LiFePO_4/C in inert atmosphere. The small amount of carbon present helps to prevent the oxidation of Fe^{2+} to Fe^{3+} [36–38] during heating in an inert atmosphere without requiring a reducing (Ar– H_2) gas atmosphere.

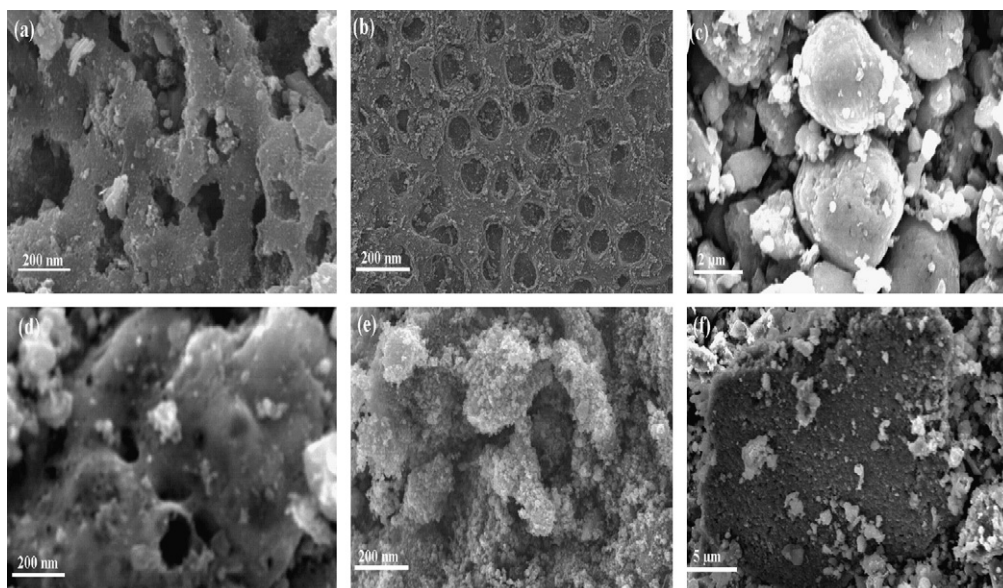


Fig. 2. SEM images of the LiFePO_4/C composites synthesized in (a–c) Ar atmosphere and (d–f) 90% Ar–10% H_2 atmosphere.

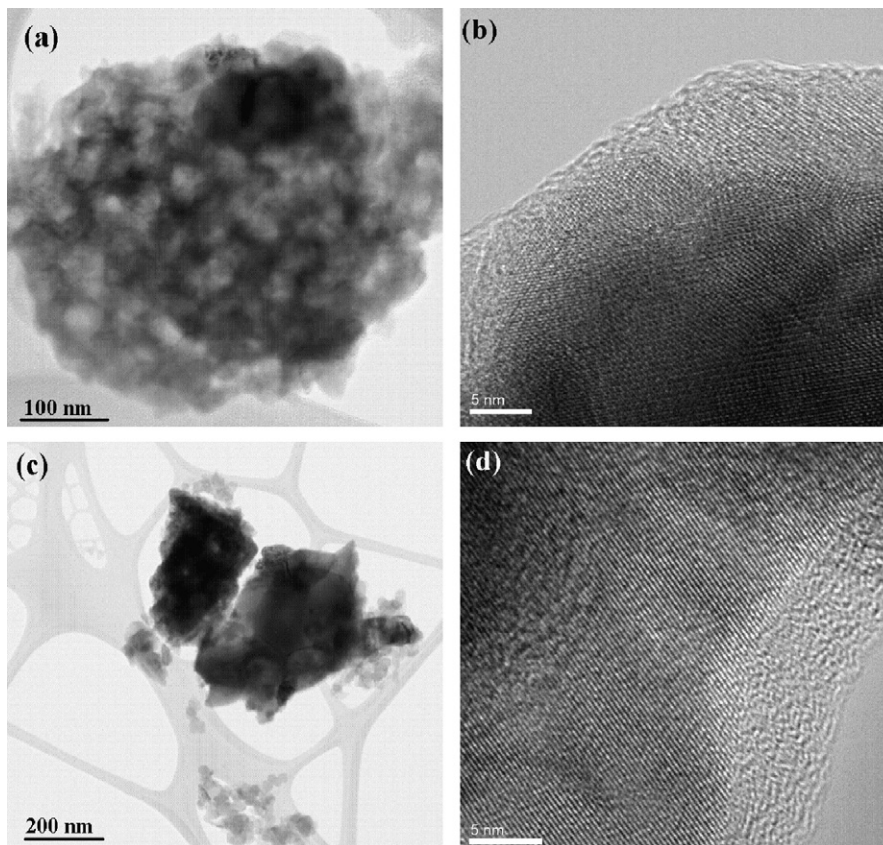


Fig. 3. TEM images of the LiFePO₄/C composites synthesized in (a and b) Ar atmosphere and (c and d) 90% Ar–10% H₂ atmosphere.

3.2. SEM and TEM analysis

Fig. 2a–f shows the SEM images of the LiFePO₄/C samples synthesized in Ar and Ar–H₂ atmospheres. The SEM data reveal the nanoporous nature of the microstructure. While a primary particle size of 5 μm is observed for the sample synthesized in Ar–H₂ mixture (Fig. 2f), a much improved porous structure with a particle size of 2 μm (Fig. 2c) is observed for the sample synthesized in Ar atmosphere. Such a symmetrically knitted porous network (Fig. 2b) observed for the sample synthesized in Ar atmosphere could facilitate an easy penetration of electrolyte and soaking of active material by the electrolyte, resulting in improved electrochemical performance.

Fig. 3 shows the TEM photographs of the samples synthesized in Ar and Ar–H₂ atmospheres. The high resolution TEM pictures clearly indicate a coating of the LiFePO₄ crystallites by carbon. Such carbon webs are known to enhance the electronic conductivity of LiFePO₄/C composite by connecting, wrapping, and existing in the interfaces between the LiFePO₄ particles [39]. Particularly, the LiFePO₄/C composite heat treated in Ar atmosphere with a reduced (100 nm) particle size (Fig. 3a) is expected to exhibit good electrochemical properties. It should be noted that the coated carbon could have come from both the added 2 wt.% Super P as well as from the carbon-containing raw materials.

3.3. Raman spectroscopic analysis

Raman spectroscopy is an excellent analytical tool [40] to confirm the presence of amorphous carbon present in the LiFePO₄/C composite cathode. However, since the high energy excitation lasers used in Raman spectroscopy could damage the LiFePO₄/C composite structure, the present study used a 514 nm laser excita-

tion. Fig. 4 shows the Raman spectrum of the LiFePO₄/C composite sample synthesized in Ar atmosphere. While the small band at 945 cm⁻¹ is attributed to the PO₄³⁻ groups, those at 1593 and 1347 cm⁻¹ are attributed, respectively, to the E_{2g} vibration mode of the ordered graphitic carbon (G-band) and the A_{1g} mode of the disordered carbon (D-band) [41,42]. The I_D/I_G intensity ratio represents the degree of surface disordering of coated carbon layer. A smaller I_D/I_G ratio of 0.8 reveals decreased level of disorder [43], which could be beneficial to improve the electrochemical properties.

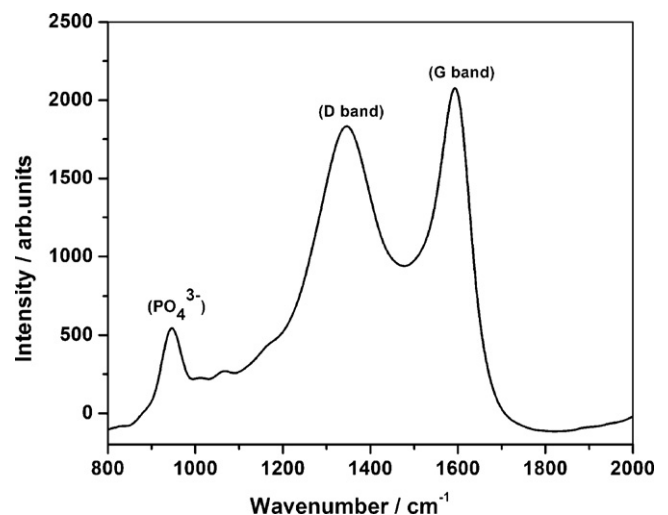


Fig. 4. Raman spectrum of the LiFePO₄/C composite synthesized in Ar atmosphere.

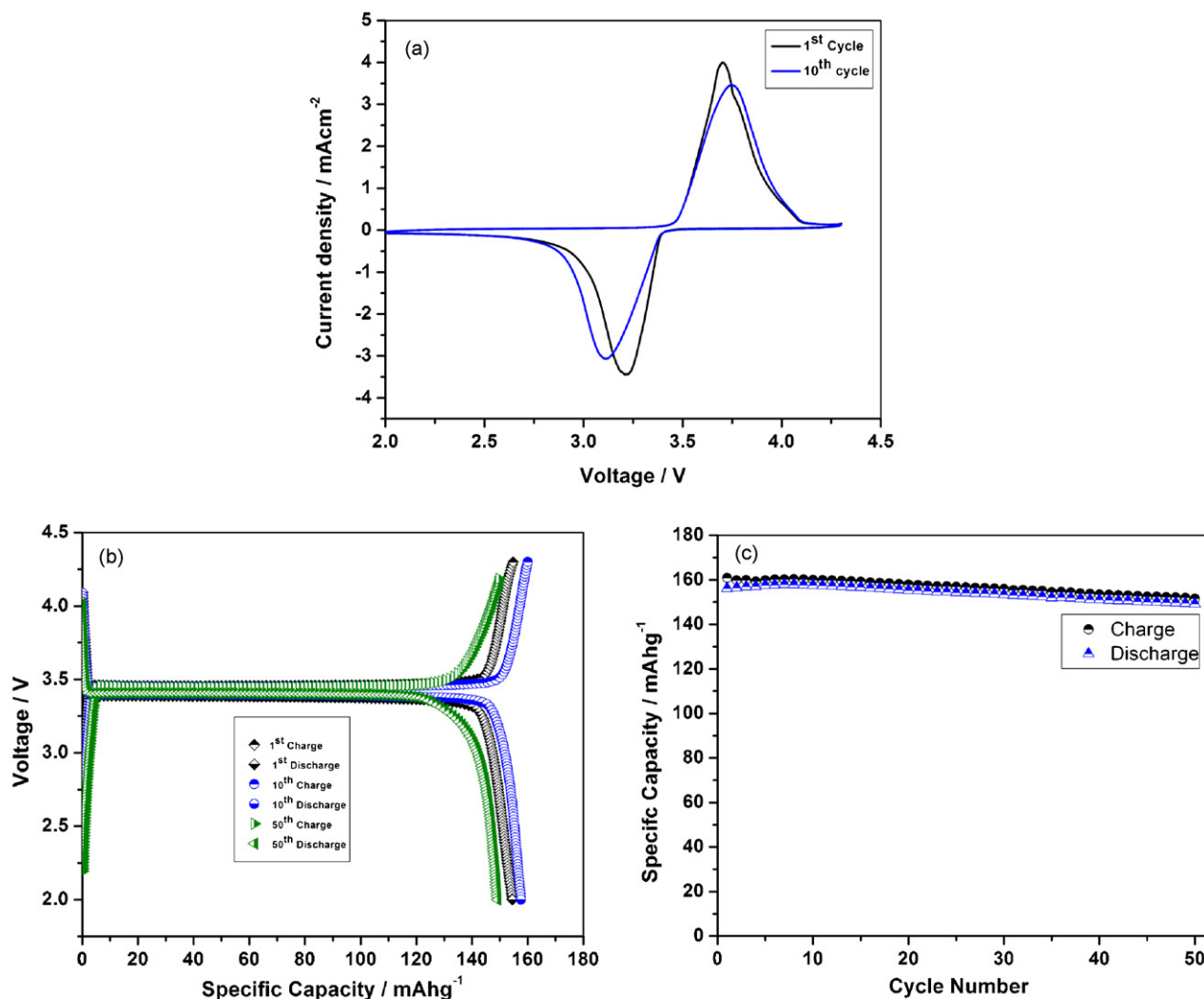


Fig. 5. (a) Cyclic voltammogram, (b) charge–discharge profiles at C/20 rate, and (c) cyclability at C/20 rate of the LiFePO₄/C composite cathode synthesized in Ar atmosphere.

3.4. Electrochemical characterization

Figs. 5a and 6a show the cyclic voltammograms recorded at a sweep rate of 0.1 mV s⁻¹ of the LiFePO₄/C composite cathodes synthesized in Ar and Ar–H₂ atmospheres. Presence of a single cathodic and an anodic peak at the respective positions confirms the occurrence of a single electron transfer reaction of LiFePO₄–FePO₄. The CV plots in Fig. 5a exhibit significantly higher intensities of cathodic and anodic peaks compared to that in Fig. 6a, indicating that the transport mechanism of Li⁺ ions and electrons is more effective in the LiFePO₄/C sample synthesized in Ar atmosphere. Moreover, the redox peaks of the 10th cycle are found to overlap with those of the 1st cycle for the sample prepared in Ar atmosphere, indicating an excellent cycling reversibility.

Figs. 5 and 6 show the charge–discharge profile of the LiFePO₄/C composite synthesized in Ar and Ar–H₂ atmospheres. The flat voltage plateau at 3.4 V indicates the two phase nature of Li⁺ extraction and insertion reaction between LiFePO₄ and FePO₄ [44]. The voltage difference between the charge and discharge plateaus of the LiFePO₄/C cathode synthesized in Ar atmosphere is negligible in Fig. 5b, indicating good lithium diffusion kinetics. On the other hand, the difference between the charge and discharge plateaus is slightly larger in Fig. 6b, indicating that the LiFePO₄/C composite synthesized in Ar–H₂ atmosphere suffers from polarization loss compared to the sample synthesized in Ar atmosphere. The larger

polarization loss of the sample synthesized in Ar–H₂ atmosphere could be related to the existence of impurity phases and slightly larger particle size as evident from the XRD and SEM data.

The LiFePO₄/C composite cathode synthesized in Ar atmosphere exhibits a discharge capacity of ~160 mAh g⁻¹ at C/20 rate with 3% capacity fade in 50 cycles (Fig. 5c). This high observed capacity value close to that of the theoretical value (169 mAh g⁻¹) reveals that the carbon content in the final product could be <5 wt.% although the carbon could have originated both from the added 2 wt.% Super P and the carbon-containing precursors. On the other hand, the sample synthesized in Ar–H₂ atmosphere exhibits an initial discharge capacity of 126 mAh g⁻¹, which increases further with progressive cycling to an extent of 143 mAh g⁻¹ at C/20 rate. Such an increase in specific capacity behavior [45,46] has been attributed to the progressively increasing surface area of the LiFePO₄/C composite cathode that results from the gradual penetration of electrolyte into the interior part of each of the particle. In contrast, the synergistic effect of carbon coating and the combustion-initiated minimization of particle size to a desired nanometric (100 nm) level offer good electrochemical performance for the sample synthesized in Ar atmosphere. The nanoporous nature of the LiFePO₄/C composite cathode synthesized in Ar not only facilitates fast Li⁺ ion and electron transport but also acts as an elastic buffer to release the strain on/from the LiFePO₄/C composite cathode during the intercalation/de-intercalation process.

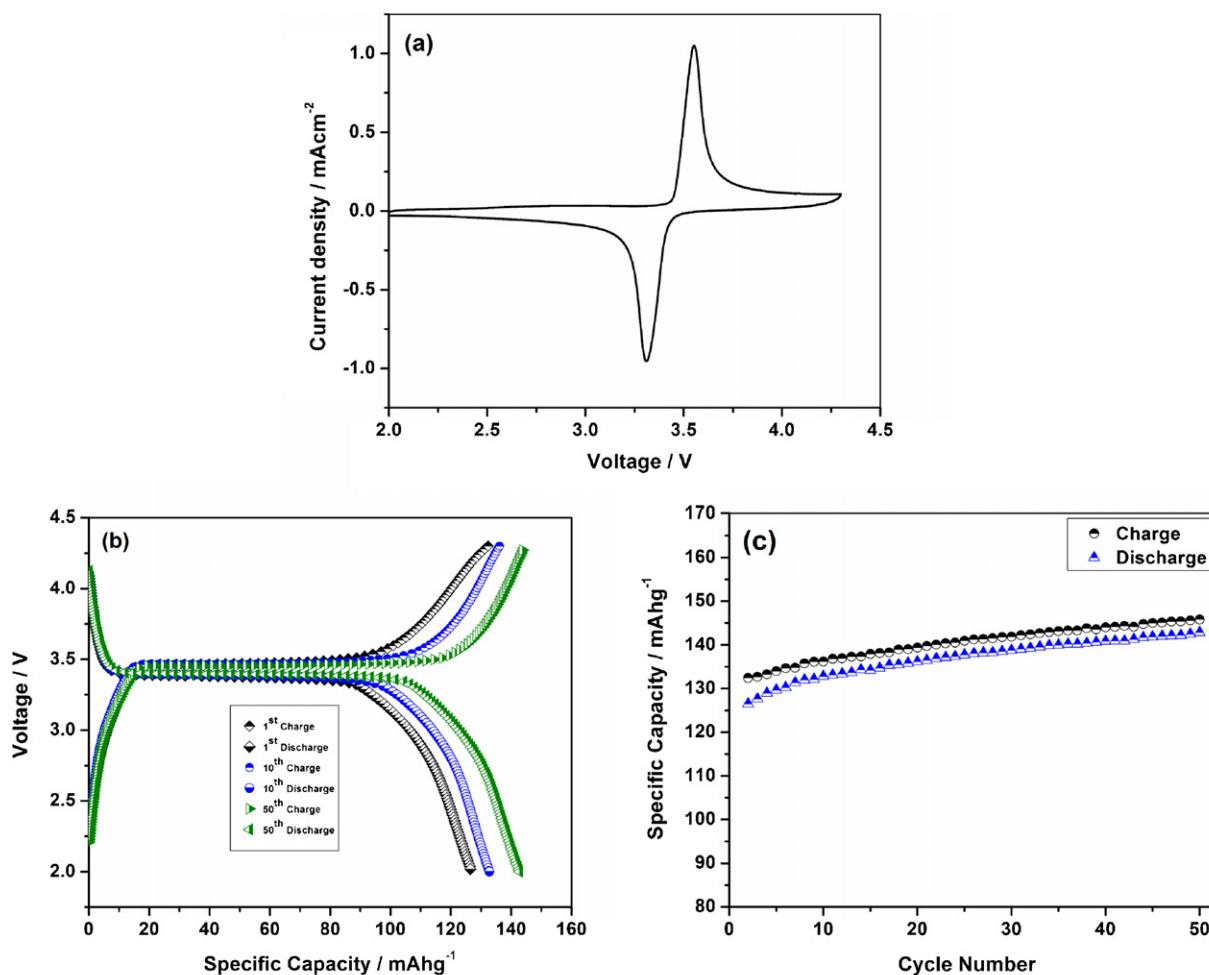


Fig. 6. (a) Cyclic voltammogram, (b) charge–discharge profiles at C/20 rate, and (c) cyclability at C/20 rate of the LiFePO₄/C composite cathode synthesized in 90% Ar–10% H₂ atmosphere.

Fig. 7 shows the rate capability of the LiFePO₄/C composite sample synthesized in Ar atmosphere. The data were collected with a fixed first charge rate of C/20 and varying the subsequent discharge–charge rates from C/20 to 2C. The discharge capacity decreases from 160 mAhg⁻¹ at C/20 rate to 122 mAhg⁻¹ at 2C

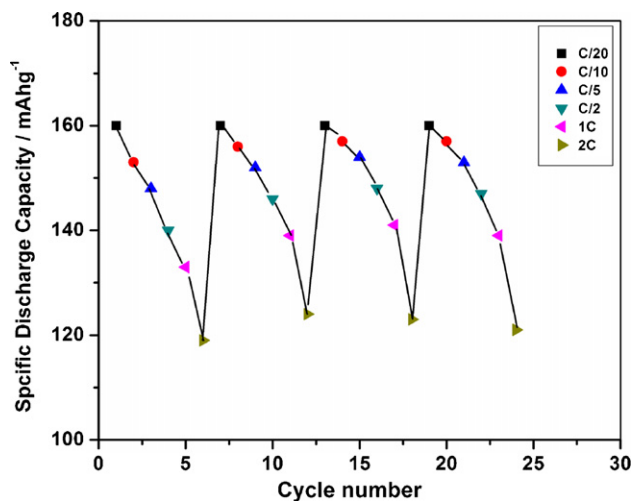


Fig. 7. Rate capability of the LiFePO₄/C composite cathode synthesized in Ar atmosphere.

rate, demonstrating excellent rate capability. The high rate capability may be attributed to the combined effect of added carbon to improve the electronic conductivity and the nanoporous network of LiFePO₄/C that allows easy percolation of electrolyte to improve the ionic conductivity. Furthermore, a high coulombic efficiency of 99% is found at both at C/20 and 2C rates.

4. Conclusions

Nanoporous LiFePO₄/C composite with facile lithium-ion and electron movement facilitated by the mesopores filled with the electrolyte has been synthesized by a glycine-assisted combustion method in presence of 2 wt.% Super P carbon by firing at 750 °C in Ar or 90% Ar–10% H₂ atmospheres for a short duration of 6 h. The Ar atmosphere gives single phase sample although the Ar–H₂ atmosphere results in the formation of trace amounts of impurity phases. While the added 2 wt.% Super P carbon is effective in impeding the grain growth and enhancing the electronic conductivity, the nanoporous nature of the LiFePO₄/C composite acts as an elastic buffer for releasing the strain during cycling and especially during high rate charge–discharge conditions. The synergistic effect of added carbon and the nanoporous network of the LiFePO₄/C composite cathode results in high capacities of 160 mAhg⁻¹ at C/20 rate and 122 mAhg⁻¹ at 2C rate with excellent cyclability and high coulombic efficiency (99%). The one-pot, GAC method presented here offers an easy and energy efficient way to produce high performance olivine LiFePO₄/C composite cathodes.

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