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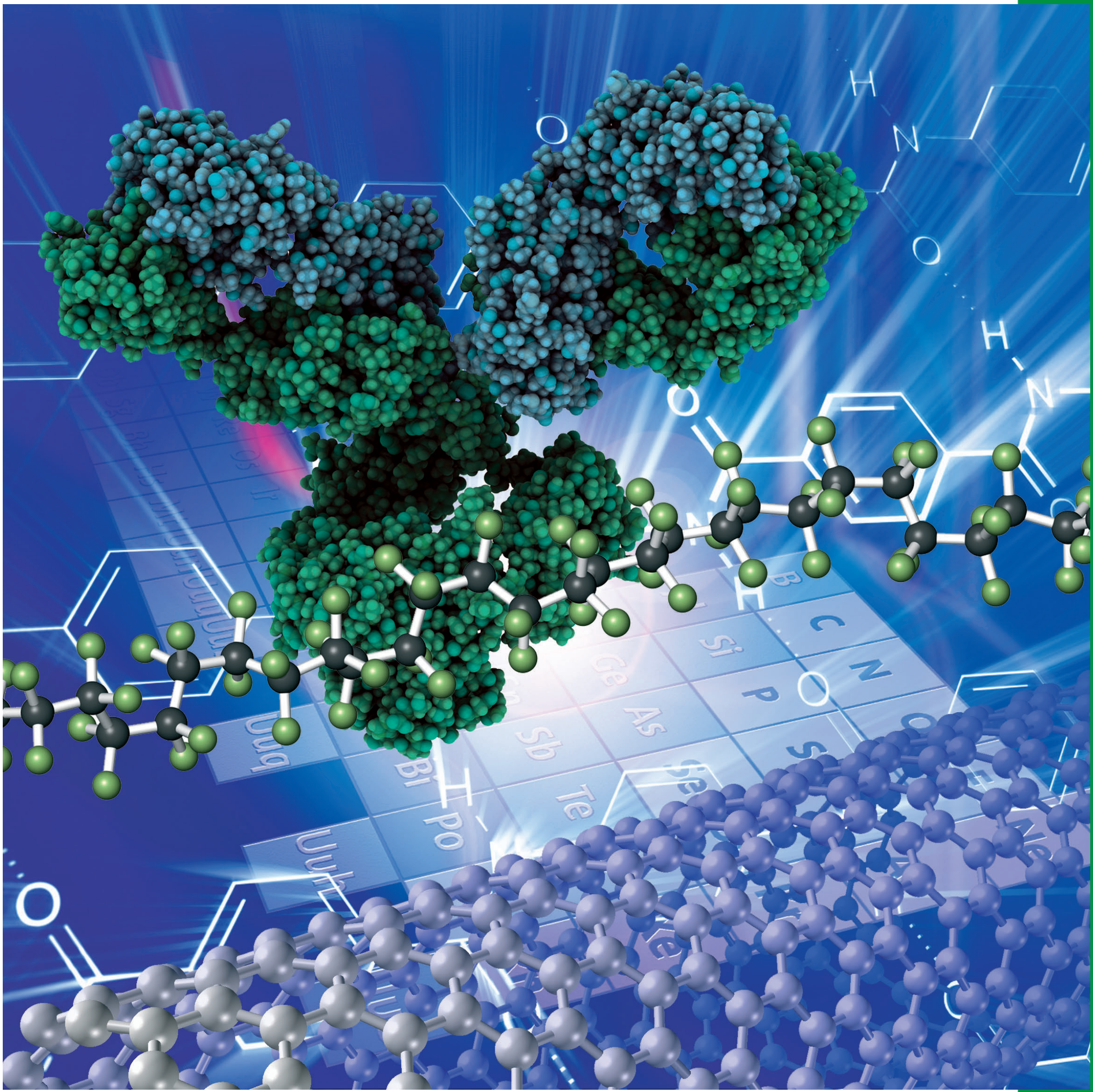

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Two Cathodes in One for Lithium-Ion Batteries: Voltammetric Study of a Composite Cathode of Sulfur and $LiFePO_4$

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In order to satisfy the growing energy demand of large-scale applications such as energy storage for renewable sources and for electromobility, advanced electroactive materials are required for energy storage technologies. The aim of this work is to develop a new cathode concept for Li-ion batteries, which allows high charging/discharging rates as well as high gravimetric capacities. The composite cathode consisting of $LiFePO_4$ (high rates) and S (high capacity), takes advantage of the benefits of both materials. However, it is a challenge considering the reactivity of both materials, and the electrolytes needed for each of them. This paper deals with some strategies to make the composite work; the problems encountered when having two materials with different electrochemical behavior in the same electrode in a battery have been partially solved. The voltammetric studies of this work show promising results for the development of the new concept of lithium-ion batteries.

1. Introduction

The lithium-ion battery technology currently used may not be enough to fulfill the energy needs of large-scale applications such electric vehicles and energy storage of renewable energy.[1,2] For instance, it is necessary to store a high energy density, and to quickly deliver it to the car engine or to the electric grid at certain times.

A good alternative are the lithium-sulfur (Li–S) batteries, which are receiving ever-increasing attention due to their high theoretical gravimetric capacity 1675 $mAhg^{-1}$, greater than any commercial lithium-ion battery. However, their rapid capacity fade has been one of the principal drawbacks for their widespread development. The working mechanism of Li-Sulfur batteries has not been completely stablished because it involves a series of chemical and electrochemical reactions, as well as the formation of soluble polysulfides intermediates.[3–6] During the charging cycle, shuttling of the polysulfides is one of the most adverse phenomena for battery performance. This process occurs when polysulfides diffuse trough the electrolyte, driven to the anode by a concentration gradient, where they are reduced.[4,7] Additionally, as sulfur is a bad electronic and ionic conductor, the charge transfer from/to the material is slow, and for this reason, high instantaneous power is not possible. One way to overcome the intrinsic problems of sulfur cathodes is to mix it with other materials in a composite. The most common material used in composite with sulfur is carbon, serving as a mechanical support, conductive additive, and to enclose S to minimize the amount of polysulfides escaping from the cathode.[8,9] In order to immobilize polysulfides, composites of sulfur with additional materials like $LiCoO_2$,[10] TiO_2[11] and MoS_2[12] have been tested.[11,12] Aiming the same purpose, composites of sulfur with polymers have also been developed.[13] However, there are no reports on sulfur composites with other active materials (materials that also store charges). In the present work we aim to combine sulfur with a material that can offer high instantaneous power ($LiFePO_4$).

$LiFePO_4$ has attracted great attention of researchers as a potential cathode material for lithium ion batteries due to its cost effectiveness, safety, environmental aspects and high instantaneous power; moreover, its electrochemical profile is very flat, located near 3.45 V versus Li/Li^+.[1] Nevertheless, the theoretical capacity of the compound is low (170 $mAhg^{-1}$).[14,15] To meet the new energy storage needs for applications like electromobility, in this work it is proposed to use functional composites of $LiFePO_4/S$ as cathode of Li ion batteries. It is intended that each of the materials of the composite contributes with their characteristic performance advantages in the new generation of lithium ion batteries. This is the first time the two materials are combined aiming to use them both as active materials; in the past, sulfur has just been just used as dopant, changing the properties of $LiFePO_4$.[16] Electrochemical evidence of the two materials actively participating as Li storage materials in a cathode is presented in this work. It is a fundamental voltammetry study that could help in the development of new high performing Li ion batteries with the new cathode concept.

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2. Results and Discussion

The composites have been tested in batteries firstly using an electrolyte with concentration 1 M of $LiPF_6$ as lithium salt in ethylene carbonate: dimethyl carbonate (EC:DMC) solvents in a 1 : 1 v:v ratio. This electrolyte was used for the first test since it is commonly used for testing $LiFePO_4$ electrodes in Li-Ion batteries. However it is widely known that carbonate-based electrolytes are bad for Li–S batteries. Cyclic voltammetry was performed at a scan rate of 100 μVs^{-1} in a voltage range of 1.3 to 4.0 V for three cycles. The voltammogram obtained is shown in Figure 1.

Peaks related with lithiation and delithiation of $LiFePO_4$, at 3.3 and 3.5 V can be clearly observed in the cyclic voltammogram of Figure 1, similarly to those reported in previous studies where $LiFePO_4$ was used as cathode material.[14] On the other hand, it is expected to observe peaks between 1.8 and 2.8 V associated to lithiation and delithiation reactions of S.[17] High-order lithium polysulfides (Li_2S_x, $4 \leq x \leq 8$) are formed at about 2.2 V in the negative voltage sweep, while low-order lithium polysulfides (Li_2S_2, Li_2S) are formed between 2.2 and 2.0 V.[4,17, 18] However, from Figure 1 it can be clearly seen that the peaks in that voltage range are of very low intensity, indicating that the activation of sulfur was not significant. The small peak close to 2.4 V could be related to the formation of a solid electrolyte interface (SEI) on the surface of the S–C composite during the first cycle, as reported for Li–S batteries using carbonate-based electrolytes.[19] The peak corresponding to the lithiation of sulfur is only observed with a zoom (inset of Figure 1) at about 2.2 V, just in the first cycle. On the other hand, a low intensity peak related to the delithiation of S can be observed at 2.46 V. It appears at a higher potential than commonly reported,[4,18] probably due to a larger charge-transfer impedance due to the incomplete dissolution of polysulfides. Additionally, it has been previously reported that polysulfides react with the carbonate-based electrolytes via nucleophilic addition or substitution reactions leading to extensive degradation of the electrolyte.[20,21]

Afterwards, the composites have been tested in half battery cells using an electrolyte commonly used in Li–S batteries, containing 0.7 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) as lithium salt in dimethyl ether : 1,3-dioxolane (DME:DOL) solvents in a 1 : 1 v:v ratio (commonly used in Li–S batteries).[4,22] Cyclic voltammetry tests were performed with this electrolyte at a scan rate of 80 μVs^{-1} in a voltage range of 1.4 V to 4.0 V. The resulting voltammogram is shown in Figure 2.

The activation of the two cathode materials can now be clearly observed in Figure 2, but only for the first cycle; the peaks rapidly fade after the first voltammetry cycle. However, there is an improvement comparing this result with the one using the carbonate-based electrolyte. During the delithiation process, the voltammogram shows an oxidation peak at about 2.5 V, indicative of a reversible reaction process of Li with S.[23] The peaks related with the lithiation and delithiation of $LiFePO_4$ also appear. The peaks tend to disappear upon cycling, probably due to the reaction of $LiFePO_4$ with the lithium polysulfides that are soluble in the electrolyte (ether-based).

To have a better insight into the potentials at which the electrochemical processes occur in this last battery, *dQ/dV* curves presented in Figure 3 were calculated from charge/discharge curves of voltage (*V*) vs capacity (*Q*). For this purpose, battery cells have been charged/discharged for 5 cycles at C/15. The *dQ/dV* curves are analog to cyclic voltammetry, with the difference that every cycle lasts the total time to lithiate or delithiate the electrode under test. Then, they are more appropriate than cyclic voltammetry to determine the existence of processes upon charge/discharge cycling. Figure 3 a and c correspond to the lithiation and delithiation of $LiFePO_4$-S/C composite during the third cycle, while graphs b and d correspond to the fifth one. Peaks related to $LiFePO_4$ and sulfur can be observed at similar potentials as in the cyclic voltammetry test of Figure 2, but with an additional peak (Z*) at about 3.4 V during the delithiation process (Figure 3 c and

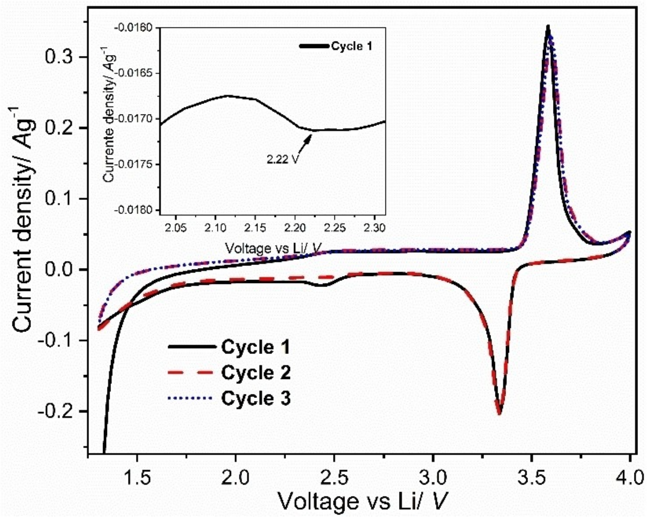

Figure 1. Cyclic Voltammetry of $LiFePO_4$-S composite with $LiPF_6$ electrolyte.

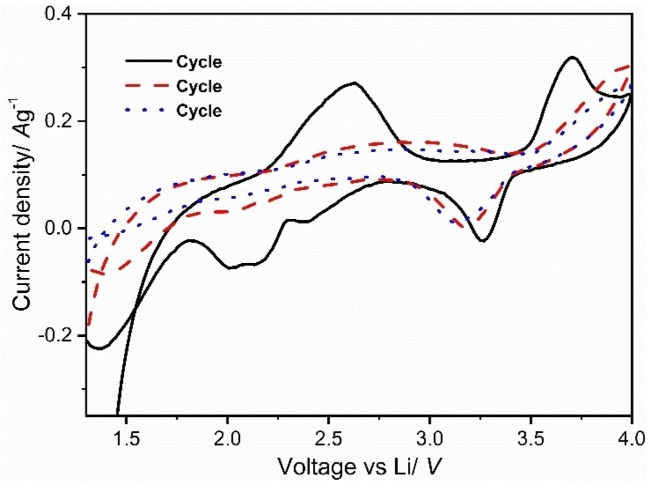

Figure 2. Cyclic Voltammetry of LiFePO4-S composite with LiTFSI electrolyte.

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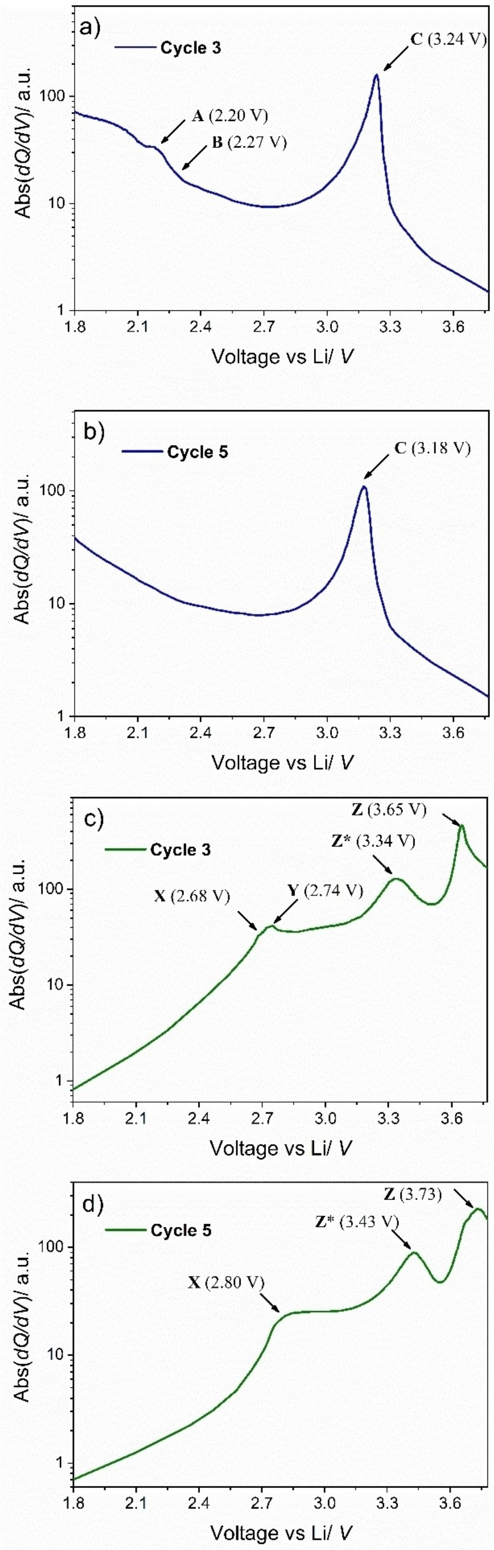

Figure 3. dQ/dV curves calculated from charge/discharge cycling data of the $LiFePO_4$-S composite cathode with LiTFSI electrolyte: Lithiation in cycle 3 (a) and cycle 5 (b), and delithiation in cycle 3 (c) and cycle 5 (d).

d). The additional peak could be related to the formation of fluorosulfates ($LiFeSO_4$-F), reported in literature at similar potentials.[24–25] They are probably produced due to the substitution of the polyanion $(PO_4)^{3-}$ by $(SO_4)^{2-}$, process that changes the olivine crystal structure. This might be caused by the migration of polysulfides, which react with $LiFePO_4$. Consequently, the peaks associated with the lithiation and delithiation of sulfur tend to disappear, and the peaks related with the lithiation and delithiation of $LiFePO_4$ suffer a voltage shift. The potential difference between the peaks of cycle 3 and cycle 5 is shown in Table 1. The lithiation peaks (at reverse voltage sweep) move to lower potentials (higher potentials vs open circuit), while the delithiation peaks (at forward voltage sweep) move to higher potentials vs Li, as a result of the increment in the overall electric resistance of the battery.

2.1. Avoiding reactions between active materials

To avoid reactions between $LiFePO_4$ and sulfur derivates, it was proposed to cover $LiFePO_4$ with some carbon. This was achieved by hydrothermal carbonization of sucrose at 180 °C in a hydrothermal reactor for 21 h, followed by a thermal treatment at 650 °C under nitrogen atmosphere. The final C/$LiFePO_4$ composite contains 30 wt% carbon. Hydrothermal carbon is commonly prepared using H_2SO_4 as reaction medium;[26–28] however, due to the oxidative nature of sulfuric acid and the possibility of $LiFePO_4$ decomposition or $LiFeSO_4$ formation, acetic acid was used instead. Figure 4 shows the morphology of the material after hydrothermal carbonization and thermal treatment. It is possible to identify clear particles ($LiFePO_4$) embedded in an electron beam - semi-transparent matrix

Table 1. Potential difference between the *dQ/dV* peaks of charging/discharging cycles 3 and 5 of batteries with the composite of $LiFePO_4$ and S/C.

Lithiation			Delithiation		
$\triangle V_A$	$\triangle V_B$	$\triangle V_C$	$\triangle V_X$	$\triangle V_Y$	$\triangle V_Z$
–	–	0.06	0.12	–	0.08

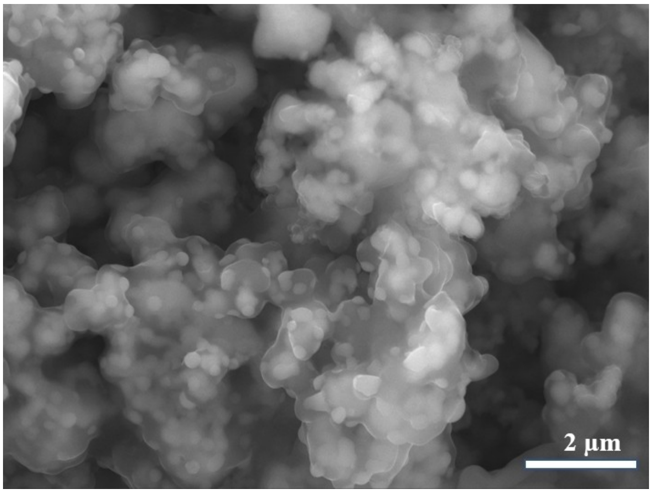

Figure 4. SEM micrograph of hydrothermal carbon - $LiFePO_4$ composite prepared in acetic acid with a further thermal treatment at 650 °C.

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(carbon). According to the XRD pattern shown in Figure 5, there was no reaction between $LiFePO_4$ and the reaction medium (the structure of $LiFePO_4$ remained intact). Furthermore, an additional peak related to graphitic carbon appears at 27° 2θ (ASTM card index PDF 00–056-0159), before and after the thermal treatment. It is important to mention that the commercial $LiFePO_4$ used for the experiments contained granulates of carbon. To prove the addition of carbon by the hydrothermal reaction, Raman spectroscopy was used. It is well known that carbon presents the Raman bands D and G at about 1300 and 1600 cm^{-1}. Band G originates from a Graphitic (laminar) ordering, and band D originates from a 3D ordering (called "Disorder", when dealing with graphitic materials).[29] As can be observed in Figure 6, $LiFePO_4$ before and after the carbonization procedure also presents these two bands. This figure shows an enhancement of graphitic band in the carbonized sample. The ratio between the areas of the bands G and D ($R = A_G/A_D$) was calculated to have a relative indication of the graphitic ordering; larger R values can be understood as higher graphitic ordering in a carbonaceous material. R amounts 0.33 for the sample without carbon coverage, while it is of 0.4 for $LiFePO_4$ covered with carbon.

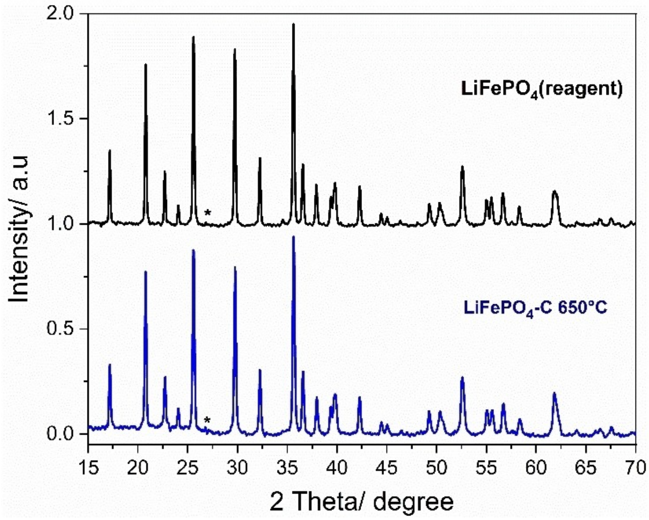

Figure 5. XRD pattern of hydrothermal carbon - $LiFePO_4$ composite prepared in acetic acid. The pattern of $LiFePO_4$ without carbon coating is shown as a reference. * Peak corresponding to graphitic carbon.

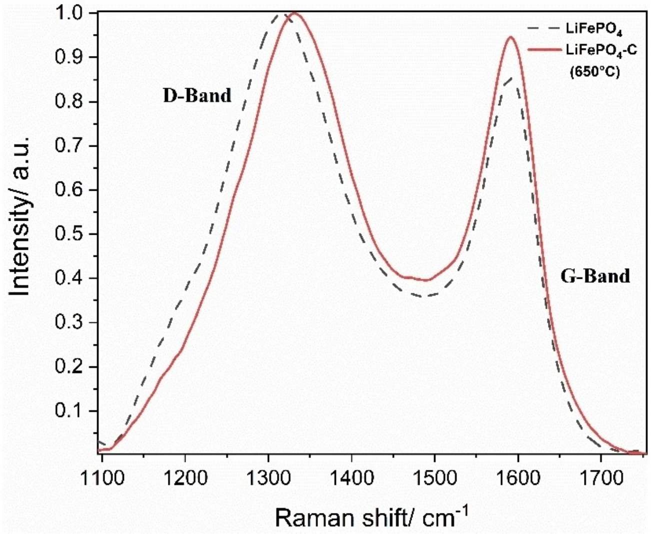

Figure 6. Raman spectrum of hydrothermal carbon-$LiFePO_4$ composite after thermal treatment at 650 °C. The Raman spectrum of $LiFePO_4$ reagent without carbon coating is shown as a reference.

In Figure 7, *dQ/dV* curves obtained from charge/discharge cycling tests of composites of S/C with carbon-coated $LiFePO_4$ are shown. As can be seen, the lithiation peaks A–B of Figure 7 a and b, related to sulfur, appear even during cycle 5. Thus sulfur lithiates and delithiates at least for 5 cycles, in contrast to the 1 cycle of the battery containing $LiFePO_4$ without carbon coverage. Furthermore, there is no peak related to the formation of fluorosulfate compounds. Nevertheless, there is a reduction in intensity of the sulfur-related peaks (capacity fade) upon cycling, indicating that sulfur is not completely retained in the carbonaceous matrix, a common problem in Li–S batteries. This problem also produces an increment in resistance of the battery, so that the Li–S reactions occur at higher potentials than expected.[30,31] However, the increment of the potential upon cycling (see Table 2) is greatly reduced compared to the composite where $LiFePO_4$ is not coated, most probably because the carbon coating minimizes the reaction of $LiFePO_4$ with polysufides and improves its electronic conductivity. A stable electrolyte in the whole potential window of the composite cathode, which additionally minimizes the diffusion of polysulfides due to its viscosity, is highly desirable to improve the performance of the batteries.

3. Conclusion

$LiFePO_4$-sulfur composites work appropriately as cathode in Li ion batteries in ether-based electrolytes (electrolytes for sulfur), but coating $LiFePO_4$ with carbon. An alternative hydrothermal carbonization process to coat $LiFePO_4$ with carbon has been developed, taking care of avoiding its chemical or thermal decomposition. Testing this material together with sulfur as a battery cathode, it could be seen that the substitution of the polyanion $(PO_4)^{3-}$ by $(SO_4)^{2-}$ in $LiFePO_4$ given by its reaction with S is avoided by the carbon coating. This allows to lithiate/delithiate S and $LiFePO_4$ independently, as demonstrated by the relatively good stability of the peaks of dQ/dV curves. This may mean that the benefits of both cathode materials, high rates and high gravimetric capacity, can be obtained in a single electrode. However, it is necessary to design new electrolytes

Table 2. Potential difference between the *dQ/dV* peaks of charging/discharging cycles 3 and 5 of batteries with the composite of carbon coated $LiFePO_4$ and S/C.

Lithiation			Delithiation		
$\triangle V_A$	$\triangle V_B$	$\triangle V_C$	$\triangle V_X$	$\triangle V_Y$	$\triangle V_Z$
0.05	0.03	0.02	0.04	0.05	0.02

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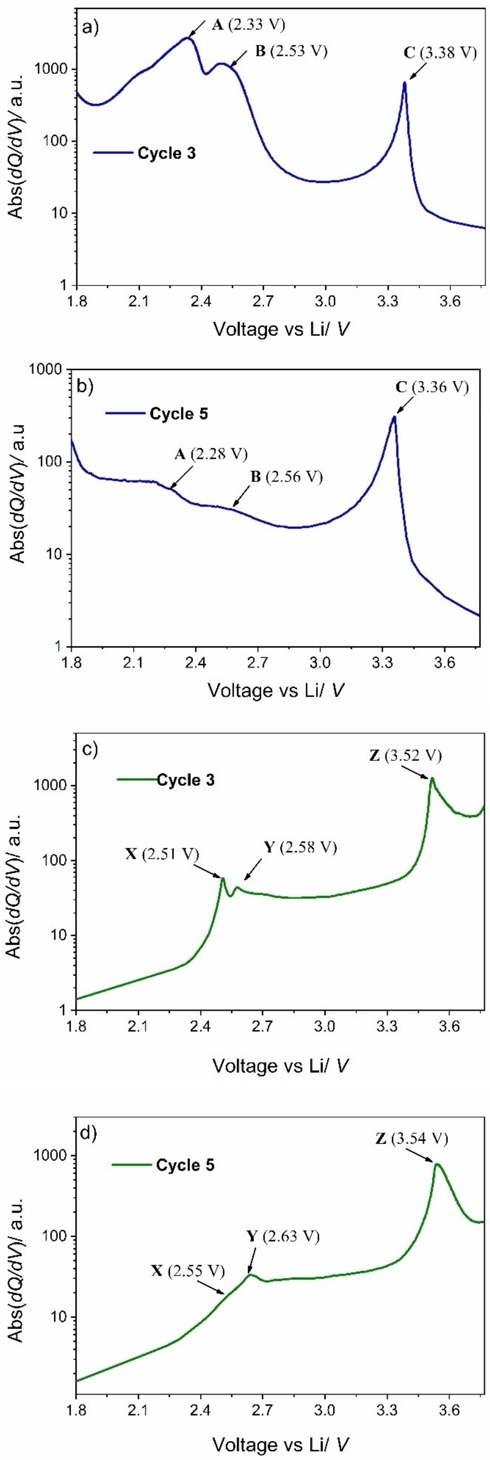

Figure 7. *dQ/dV* curves calculated from charge/discharge cycling data of composite cathodes of carbon-coated $LiFePO_4$ (prepared in acetic acid) and sulfur infiltrated in porous carbon: Lithiation in cycle 3 (a) and cycle 5 (b), and delithiation in cycle 3 (c) and cycle 5 (d).

for this special battery concept. This is the first time that sulfur is combined with another active material in the same cathode.

Supporting Information Summary

The detailed experimental details can be found in Supporting Information.

Declaration of competing interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Composite cathode · Hydrothermal synthesis · Electrochemistry · Lithium-Sulfur battery · Two cathodes in one

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