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HOW TO ELECTROCHEMICALLY STORE POTASSIUM IN SELENIUM

Tesi di laurea sperimentale

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1 Abstract

Potassium-selenium (K-Se) batteries are an interesting alternative to lithium-selenium (Li-Se) batteries with some notable advantages, such as a reduced cost of production and an environmentally cleaner way of production. Although the idea of K-Se batteries emerged a couple of years ago, in the last few years they have been taken seriously as a capable energy storage. Despite some disadvantages, such as a cathode volume expansion and the shuttle effect, it is considered as an interesting research field and many studies have been carried out. Herein, a carbon host to encapsulate selenium was made to try to reduce the shuttle effect. The defects in the carbon host will be controlled by H_2O_2 and the products will be analyzed to understand the correlation between the amount of H_2O_2 and the defects. After encapsulating selenium, the electrochemical properties will be analyzed using cyclic voltammetry, galvanostatic charge/discharge. (Additionally, the influence of the concentration of electrolyte will be studied due to it can modify the electrochemical properties of the batteries). The present project aims to determine if there is a considerable influence on the battery performance owing to the defects of the carbon hosts and the concentration of the electrolyte, and hence to find the best working condition both for K-Se batteries and for the encapsulation.

2 Introduction

Li-ion batteries (LIBs) have been used as a rechargeable electronic device since their introduction into the energy storage market in 1990s, and they have become necessary for the everyday life, due to their use in all electronic devices. To date, researchers from all over the world have been trying to develop a different kind of energy storage due to some disadvantages that LIBs have. First, lithium-Ion batteries have short life of 2 to 3 years from the date of manufacture, irrespective of their use, or absence of it. Secondly, they degrade much faster if they are exposed to heat as compared to the normal temperature exposure because they are extremely sensitive to high temperatures. Third, LIBs are ruined if they are completely discharged, and the cost of Li is particularly high compared to other kind of metals and it is going to further raise up due to its constantly usage. Finally, there may be a small risk that LIBs get busted into flames if they are not properly manufactured: to date it has been calculated that about 2 to 3 packs per million batteries produced may be defective [1].

Potassium-Selenium batteries (K-Se) are seen as an alternative to LIBs; the potassium ions react with the Se through a conversion reaction, giving K_2Se as a product.

Potassium has been chosen as an anode due to its promising electrochemical properties. Indeed, its standard electric potential ($K^+/K = -2.93$ V vs SHE) is similar to the lithium one ($Li^+/Li = -3.04$ V vs SHE) and lower than the other alkaline metals ($Ca^{2+}/Ca = -2.87$ V; $Na^+/Na = -2.71$ V, $Mg^{2+}/Mg = -2.27$ V vs. SHE), [2] which gives the opportunity to build batteries with a high energy density and voltage. The use of Se as a cathode material is given by its higher electrical conductivity, its volumetric capacity and its power densities. All these properties make Se a suitable element for a cathode material [3].

The build of a cell is similar to that of a LIB: a potassium anode is separated from a selenium cathode with a separator and the electrolyte. The K^+ ions migrate from the anode to the cathode, subsequently they react with the Se atoms at the cathode during the discharge process and they migrate back to the anode during the charge process.

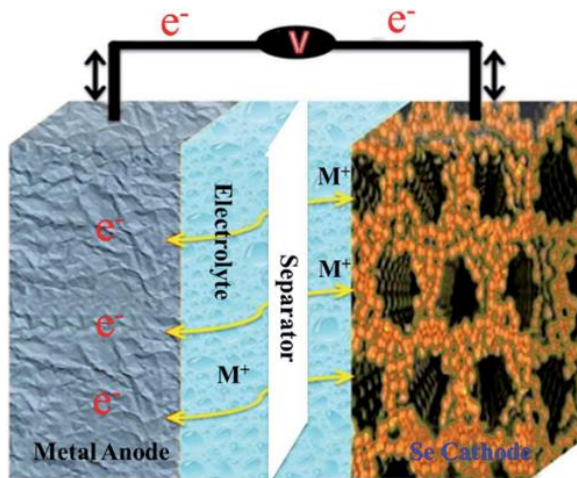


FIGURE 1 A SCHEMATIC DIAGRAM OF RECHARGEABLE METAL BATTERIES BASED ON SE CATHODES

One of the main issues that need to be solved to improve the capacity of the K-Se batteries is the formation of polyselenides and the consequent shuttle effect. This occurs due to the formation of soluble potassium-selenium compounds during the conversion reaction, which causes a loss of capacity. It has been demonstrated that Selenium is first reduced to K_2Se_n ($n > 4$), which is then further reduced to K_2Se_2 and K_2Se after discharging. During the charge reaction, K_2Se is directly oxidized to K_2Se_n ($n > 4$) and then Se. The formation of K_2Se_n can bring to the formation of soluble compounds that can dissolve into the electrolyte and, consequently, there is a loss of active material that causes, as mentioned before, a loss of capacity in the battery.

To overcome this issue the researchers have been focused on two points: either it is possible to work on the electrolyte, trying to find one that is not only a good potassium ion conductor, a good electron insulator but also that does not solubilize the polyselenides, or it has been found that if the selenium is trapped into a matrix into the cathode using a nano carbonate structure, the phenomena of the polyselenides is less likely to occur. Subsequently the shuttle effect can be avoided. Also, the use of a carbon-based matrix for the cathode can improve the efficiency of the active materials since the carbon is a good conductor and it has good electrochemical properties.

The carbon hosts that can be used as a matrix for a Se cathode can be divided in 5 different categories:

2.1 Porous carbon-selenium cathode

Porous carbon materials are among the most widely used hosts to encapsulate selenium, due to their high conductivity and large pore volumes. The porous material not only prevent the Se atoms from leaving the cathode, but also can promote the movement of electrons and potassium ions in the composites. In short, selenium molecules can be hosted in two different porous structures: the microporous and the mesoporous. The difference between them is just the size of the pores: the first ones are smaller than 2 nm and the second ones have a size between 2 and 50 nm. As for the proprieties of the different size of the pores, it can be said that the micropores can effectively restrict the dissolution of polyselenides owing to volume constrains, the mesoporous with small pores accommodates the selenium and restricts the dissolution of polyselenides, while mesoporous with larger pores can enhance the amount of selenium that can be accommodated so the electrolyte can infiltrate more efficiently [4] (FIGURE 2).

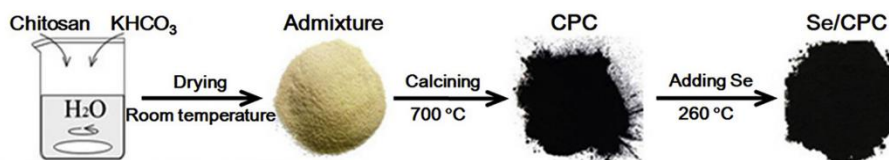


FIGURE 2 SCHEMATIC ILLUSTRATION OF THE PREPARATION POROUS CARBON MATRIX

2.2 One-dimensional carbon-selenium cathode

One dimensional carbon is extremely attractive since the special one-dimensional character can not only accommodate volume expansion without pulverization but can also facilitate axial charge transport and short radial K-ion diffusion [5] (FIGURE 3).

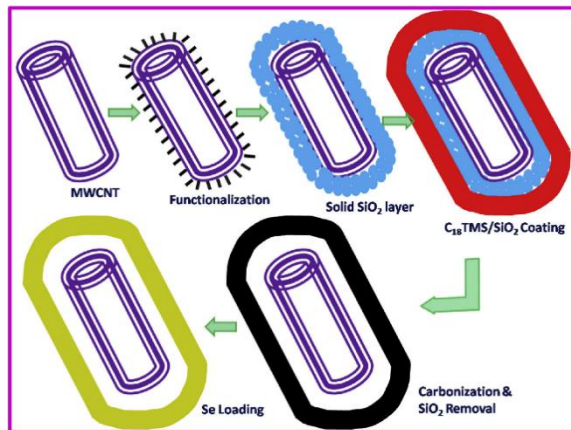


FIGURE 3 STEPS INVOLVED IN THE SYNTHESIS OF TTC/SE-X COMPOSITES.

2.3 Two-dimensional carbon selenium cathode

Two typical two-dimensional carbon conductive materials are graphene, graphene oxide (GO) and reduced graphene oxide (RGO). They can be combined with particles of group-16 elements, such as Se, to prevent the dissolution of intermediate species, such as polyselenides, thereby resulting in the formation of a highly conductive electrical path for the active materials [6] (FIGURE 4).

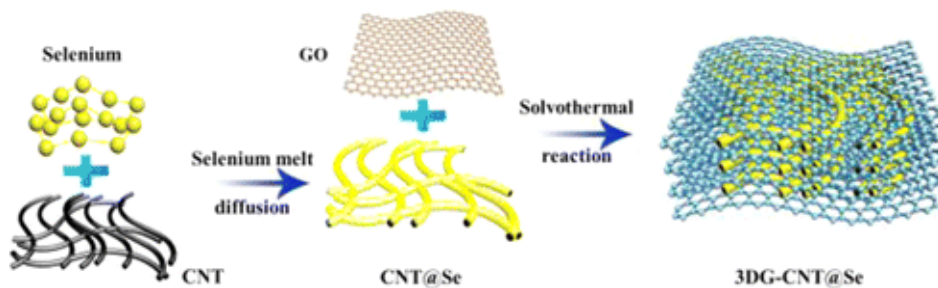


FIGURE 4 SCHEMATIC ILLUSTRATION OF THE SYNTHESIS PROCEDURE OF THE 3DG-CARBON NANOTUBES@SE COMPOSITE

2.4 Three-dimensional carbon materials

Three-dimensional carbon materials owing to their unique hollow structure, on the one hand they can provide enough buffer volume for the Se cathode during the charge/discharge process; on the other hand, they intensively restrict the dissolution of polyselenides [7] (FIGURE 5).

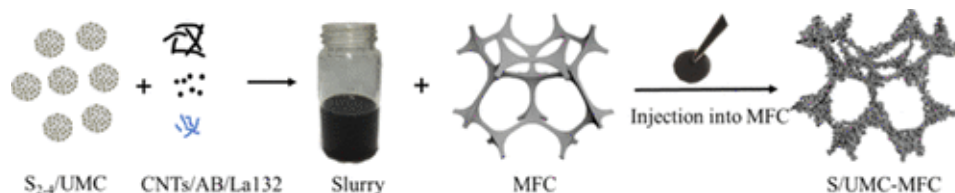


FIGURE 5 SCHEMATIC ILLUSTRATION OF THE PREPARATION PROCESS OF S₂₋₄/UMC-MFC ELECTRODE WITH HIGH SULFUR LOADING

2.5 Heteroatom-doped carbon selenium cathode

Heteroatoms doped in carbon materials can be used to further improve the electrochemical performance of M–Se batteries. They can assist in forming carbon functional group–selenium bonds, which hinder polyselenide shuttling. At the same time, they can enhance the conductivity of the carbon host and increase the reaction active sites. One of the most used atoms to dope the carbon hosts is nitrogen [8].

Concluding, encapsulation of Se in a carbon host has been proposed as a strategy to overcome the issues in K–Se batteries. Many types of hosts have been used such as porous carbon or one/two/three-dimensional carbon. The porous material not only prevent the Se atoms from leaving the cathode but also can promote the movement of electrons and potassium ions in the composites.

Concluding, selenium molecules can be hosted in different matrixes that have different microstructures: the microporous and the mesoporous. For what concern the proprieties of the different size of the pores it can be said that the micropores can effectively restrict the dissolution of polyselenides owing to volume constrains and the mesoporous with small pores accommodates the selenium and restricts the dissolution of polyselenides, while mesoporous with larger pores can

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enhance the amount of selenium that can be accommodated so the electrolyte can infiltrate more efficiently.

This work was aimed to synthesize a porous carbon matrix and encapsulate the Se inside using a vacuum annealing technique. A hydrothermal reaction has been used, adding different amount of peroxide in order to etch the carbon atoms and consequently make defects into the matrix. This project aimed to take a successful and previous experiment done for lithium-sulfur batteries and to prove the efficiency of a porous matrix not only for lithium-sulfur batteries but also for K-Se batteries. It has been expected to optimize the encapsulation condition for this reaction and to try to understand the relation between the matrix properties, the encapsulation results and the electrochemical properties this matrix could have.

3 Experimental part

Synthesis of defective carbon black

Commercial carbon black was dispersed into a mixed solution of H₂O and ethanol with a volume ratio of 1:1 under ultra-sonication. Then 0.25, 0.5, 1, 2.5, 4, 5 mL of H₂O₂ are added to modify the defectivity of carbon black. After magnetic stirring, the suspensions are transferred into a Teflon sealed autoclaves and heated at 200 °C for 6h, respectively. After cooling down, the final black solid products are obtained by filtering the suspensions, followed by vacuum drying, and denoted as CB-1, CB-2, CB-3, CB-4, CB-5, and CB-6 respectively.

Preparation of Se cathodes

The selenium has been encapsulated inside the matrixes using a vacuum annealing technique. The sample was put into a glass tube with the Selenium with a defined ratio between them (10⁻¹ mbar). Then, using a Schleck line, a vacuum inside the tube was made (FIGURE 6) and afterwards the sample was sealed using a torch flame, put into a furnace and heated at 300°C for 18h.

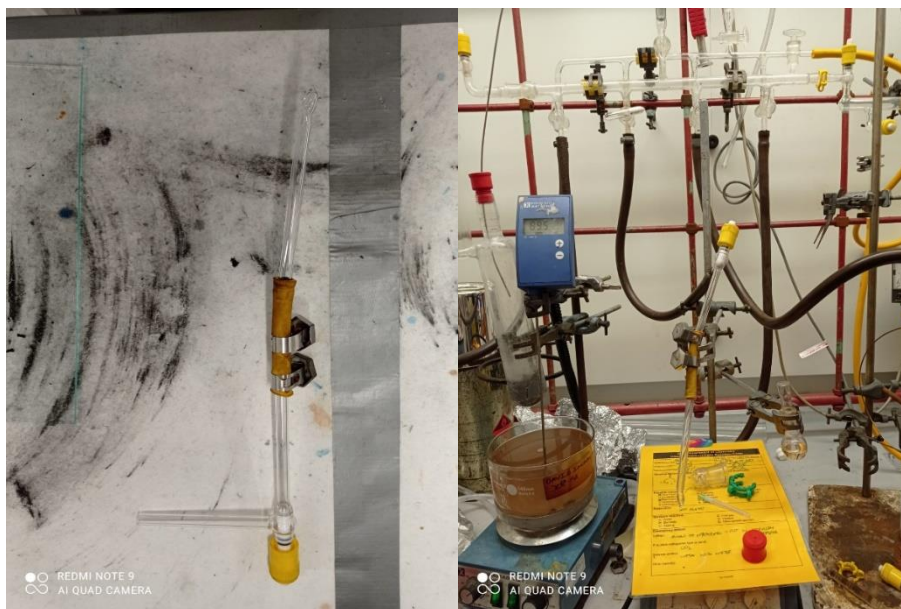


FIGURE 6 TOOLS USED TO ENCAPSULATE SE THROUGH VACUUM ANNEALING

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Material Characterization

Characterization of the nanowires was carried out by X-ray diffractometry (XRD, D/MAX2500 V PC diffractometer, Mo K α λ = 0.70930 Å), scanning electron microscopy (SEM, Hitachi S4800), Raman spectroscopy and TGA. These techniques were used to analyze the morphology, crystallinity and composition of the samples.

Electrochemical Measurements

The working electrodes were produced by mixing CB-1,2,3,4,5 with Super P and carboxymethyl cellulose (CMC) in the weight ratio of 7:2:1 respectively with a few drops water. The slurry was coated uniformly (doctor-blade) on a copper foil and dried at 100 °C under vacuum for 10 hours. The coin cells were assembled in an argon-filled glovebox with oxygen and moisture concentrations being kept below 0.1 ppm. K metal was used as the counter electrode, which was separated from the working electrode by a layer of glass microfiber filter (Whatman, Grade GF/B). The carbonate electrolyte was 1 M potassium bis(fluorosulfonyl)imide (KFSI) in an ethylene carbonate (EC)/diethylene carbonate (DEC) solution (1:1) and 7 M KFSI in dimethoxyethane (DME). Galvanostatic charge and discharge analyses were performed on a Neware battery testing system at current densities of 50-1000 mA g^{-1} at room temperature.

4 Results and Discussion

The aim of the experiment was to investigate the electrochemical properties of Selenium encapsulated into a carbon matrix. Six different carbon matrixes have been made with six different amounts of peroxide added in order to make defects into the carbon matrix as shown in Table 1.

TABLE 1 SUMMARY OF THE SAMPLES WITH THE AMOUNT OF PEROXIDE ADDED

MATRIX	AMOUNT OF PEROXIDE	NAME
Carbon	0.25	CB-1
Carbon	0.5	CB-2
Carbon	1	CB-3
Carbon	2.5	CB-4
Carbon	4	CB-5
Carbon	5	CB-6

MATRIX CHARACTERIZATION

First, the matrixes were analyzed through SEM and Raman. The first analytical method was used to see if there were any visual differences between the matrixes, and the second one to understand the level of defectivity inside the carbon matrix.

SEM

As it is possible to notice there are no significant differences between the matrixes (Fig. 7); the black spots have been assigned to the carbon tape that has been used to put the sample on and the white spots have been assigned to the gold has been used to improve the quality of the image.

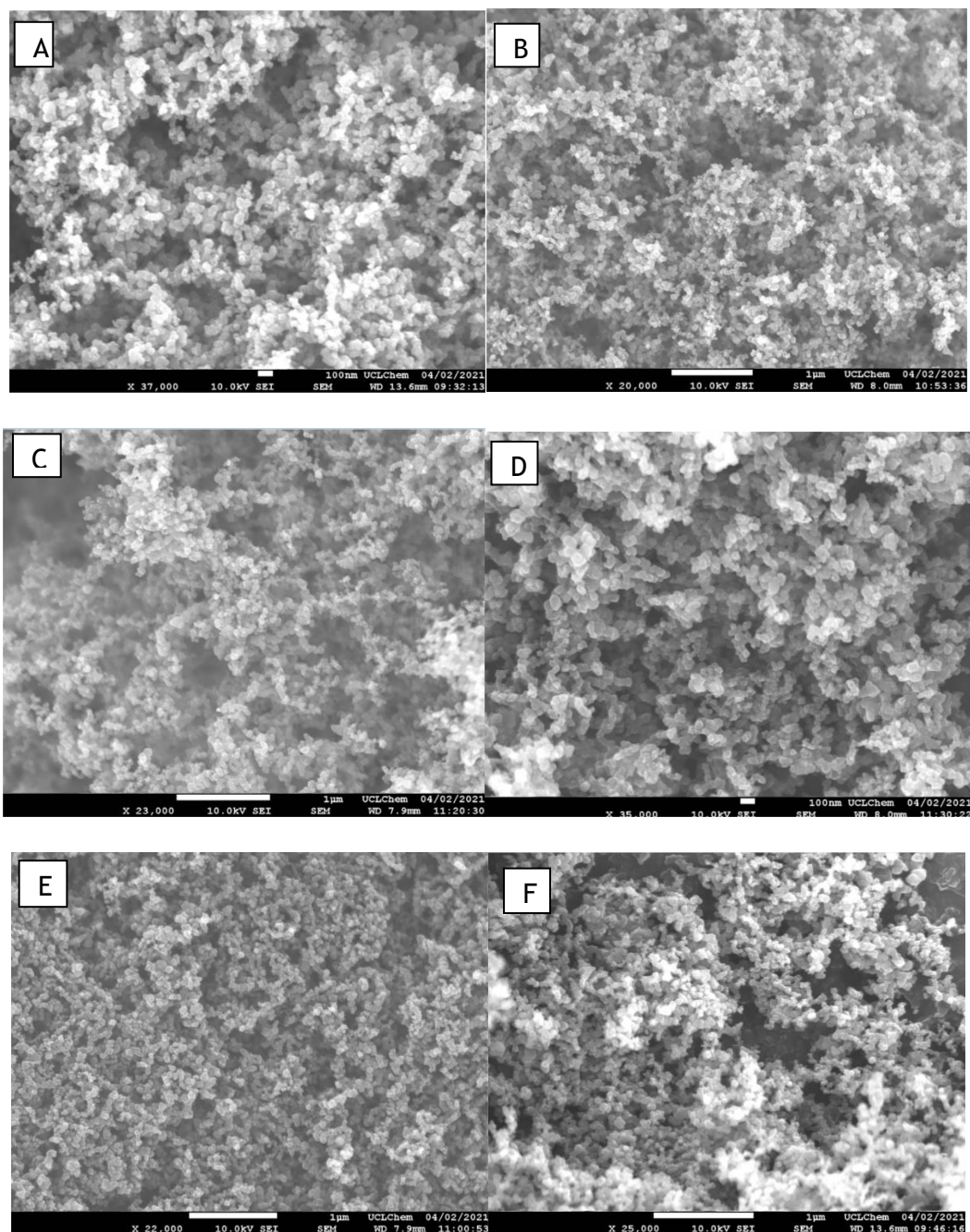


FIGURE 7 SEM IMAGES OF CB-1 (A), CB-2 (B), CB-3 (C), CB-4 (D), CB-5 (E), CB-6 (F)

However, it is possible to confirm the carbon kept its peculiar porosity in every sample and consequently it did not undergo any polymerization reaction.

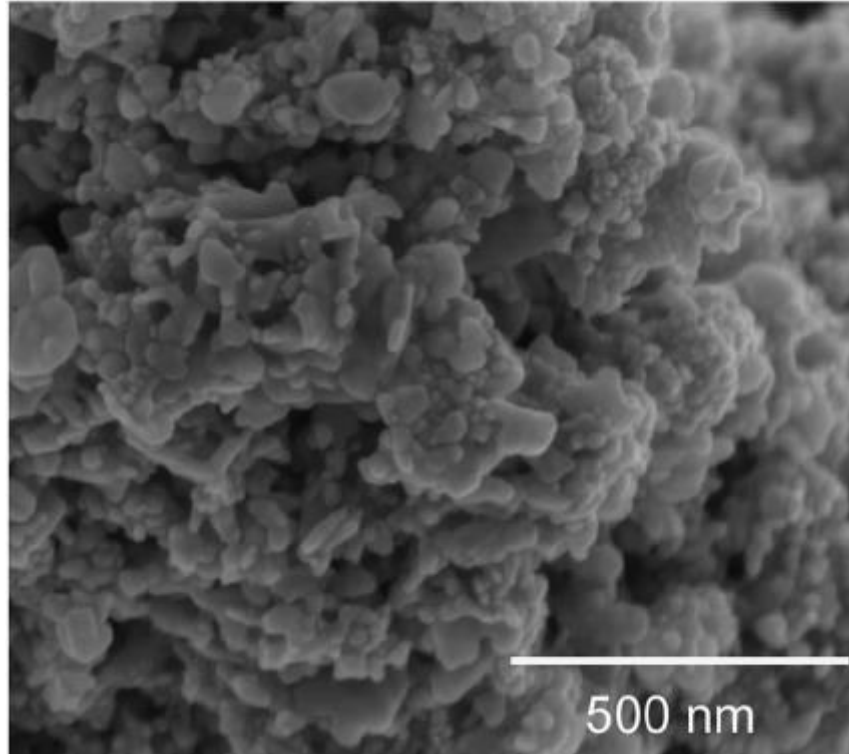


FIGURE 8 SEM CARBON BLACK [9]

Confronting the images taken for the samples e with the SEM image of the carbon black (FIGURE 8) it is possible to notice that no significant differences can be found. The porosity of the carbon black was found also in CB-1,2,3,4,5,6.

RAMAN

Raman analysis was carried out in order to detect the level of the disorder of the carbon. The Raman carbon spectrum usually shows two characteristic bands called D and G; the first one, around 1400cm^{-1} , the second one, located around 1600cm^{-1} . A D-band being present is associated with the disorder level of the crystal structure with a lower symmetry of the sp^2 carbon. The G band, is assigned to ‘in plane’ displacement of the carbons strongly coupled in the hexagonal sheets. When disorder is introduced into the graphite structure, the bands change their intensity (I). The ratio between I_G/I_D can give an information about the difference of level of atomic defects

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within the samples. It should be noted that high usage of peroxide is favorable for generating more holes and edges, resulting in the deposition of abundant defect sites on CB. However, the excessive peroxide may cause the surface reconstruction, thus leading to the formation of another ordered structure and resulting in increase of I_g/I_d intensity ratio [10].

Four matrixes (CB-1, CB-2, CB-5, CB-6) have been analyzed in order to define a trend (FIGURE 9).

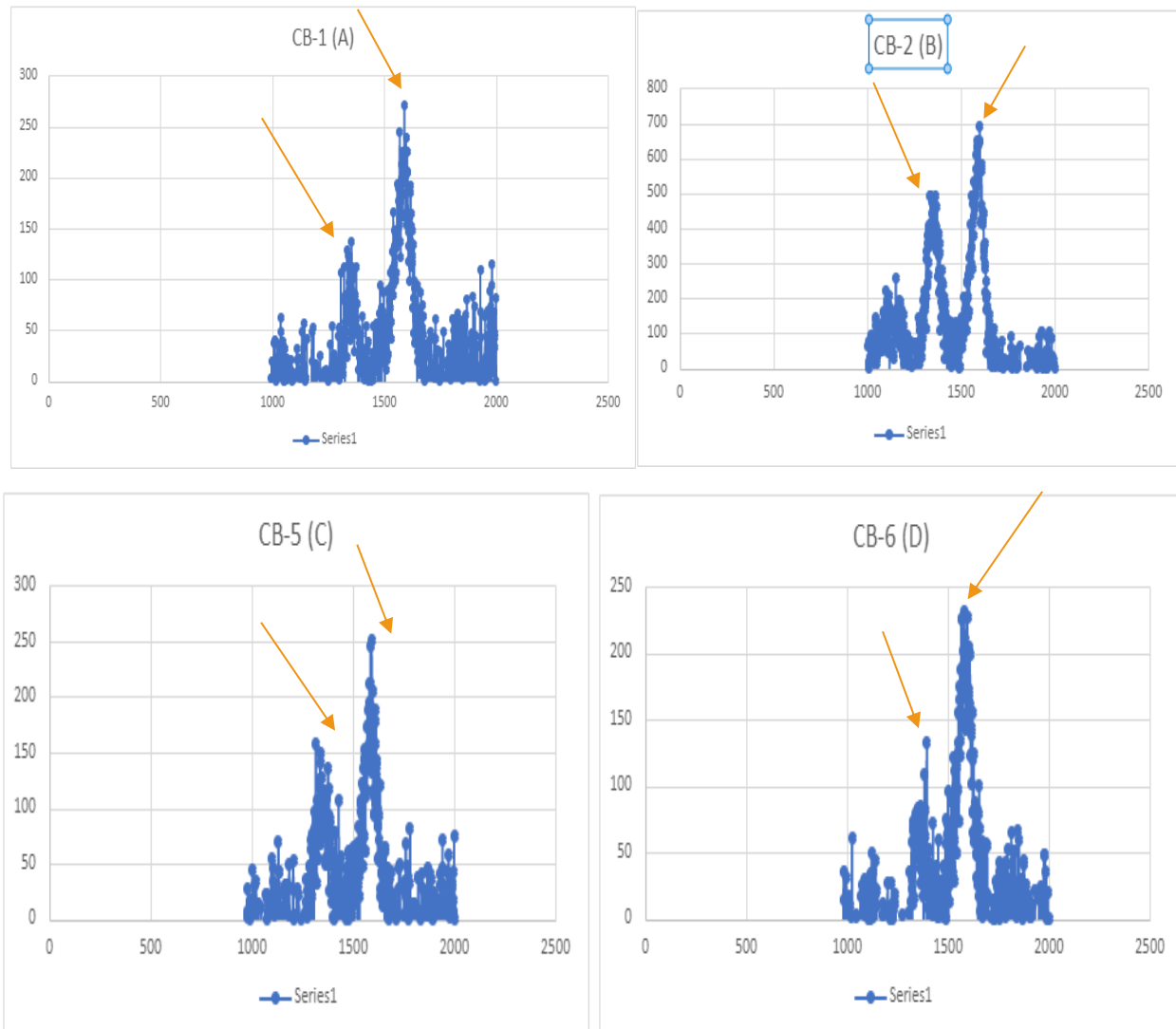


FIGURE 9 RAMAN CB-1 (A), CB-2 (B), CB-5 (C), CB-6 (D)

The ratio defined between D and G in CB-1 is 2.245, in CB-2 is 1.38, in CB-5 is 1.88 and in CB-6 is 3.26. It is possible to notice and define that the ratio initially decreases from CB-1 to CB-2 and then it increases again. As mentioned before a small amount of added peroxide may create defects at atomic level resulting in an increase of the intensity of the D band, but a higher amount of peroxide may lead to reconstruction of the surface leading to a decreasing of the D band and consequently to an increase of the ratio between the two bands.

ENCAPSULATION CHARACTERIZATION

The first aim of the encapsulation was to find the optimum ratio for it. To this end, the CB-6 matrix has been used and different ratio between Selenium and the carbon matrix have been made as shown in Table 2.

TABLE 2 DIFFERENT RATIO OF SE USED

Amount of CB-6	Amount of Se	Ratio
1	1	1:1
1	2	1:2
1	3	1:3
1	4	1:4
1	6	1:6

Subsequently, all the samples encapsulated were analyzed with SEM and EDX to see differences within them, such as the presence of big chunks of Se, that may then affect the outcome of the conversion reaction in the battery.

The goal of this analysis was to first visually compare all of the samples in order to define any differences within them, and, more important, to detect any presence of Se chunks inside the samples. When the vacuum annealing reaction doesn't undergo correctly it is possible to notice that the porosity of the matrix, in certain points of the sample, turns into a smooth surface, typically

connected to selenium. All the selenium, if correctly annealed should be inside the matrix and so the pictures taken with the SEM of the samples encapsulated should be very similar to the pictures taken before the encapsulation.

Different sites were considered in order to have information more in detail about the uniformity and the presence of Se into the sample.

- CB-6(1:1)

As it is possible to see in FIGURE 10 the SEM did not show any presence of big chunks of Se, all the images show a porous surface that can be assigned to the carbon matrix. However, the EDX showed the presence of Se inside the sample. It is possible to deduct that the selenium has been successfully encapsulated inside the matrix.

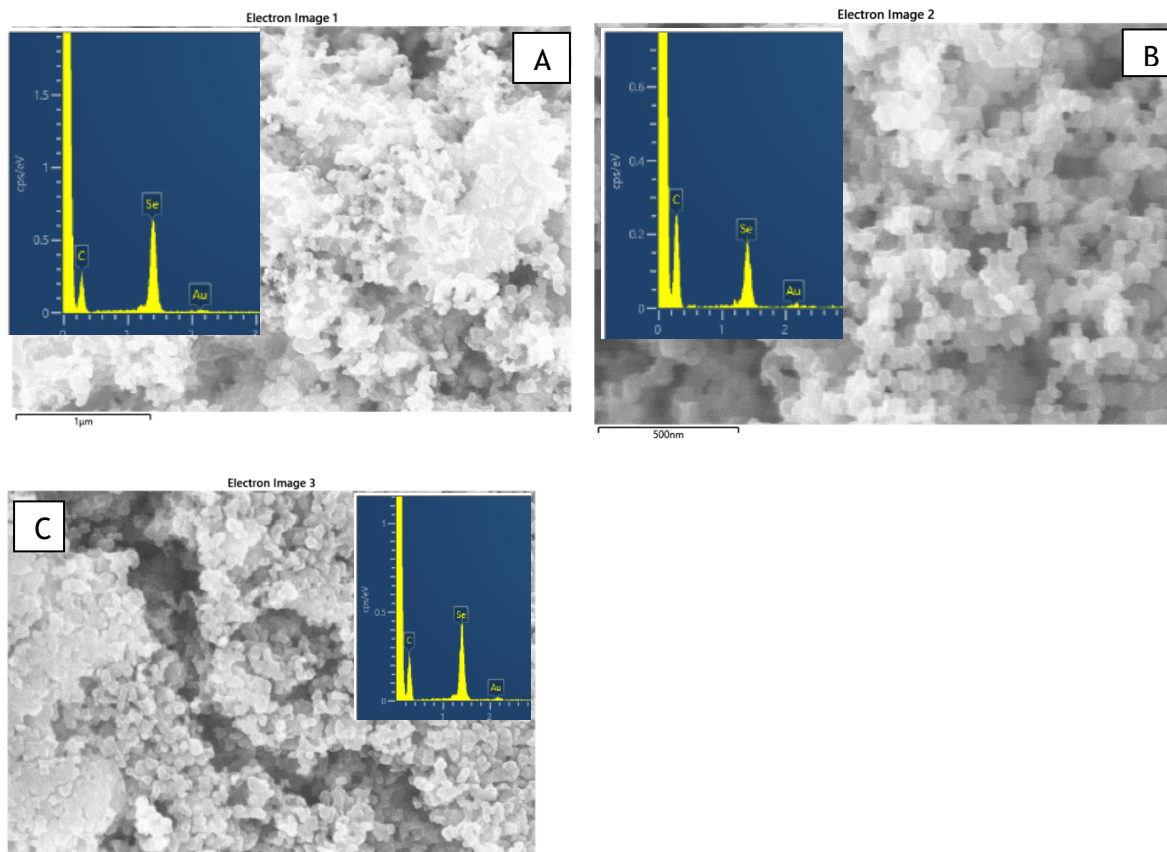


FIGURE 10 SEM AND EDX OF CB-6 1:1, SITE 1 (A), SITE 2 (B), SITE 3 (C)

-CB-6(1:2)

In this sample (FIGURE 11) it is possible to detect a chunk of Se (FIGURE 11B), the image does not show the typical porosity of the carbon, but it shows a smooth surface, usually sign of a selenium chunk. However, in site 1 and 3 (FIGURE 11A and 11C) the EDX shows important selenium peaks and in the relatives SEM images there are no presence of Se chunks. In conclusion, the CB-6(1:2) ratio showed a slightly presence of chunks of Se but most of the Se was encapsulated.

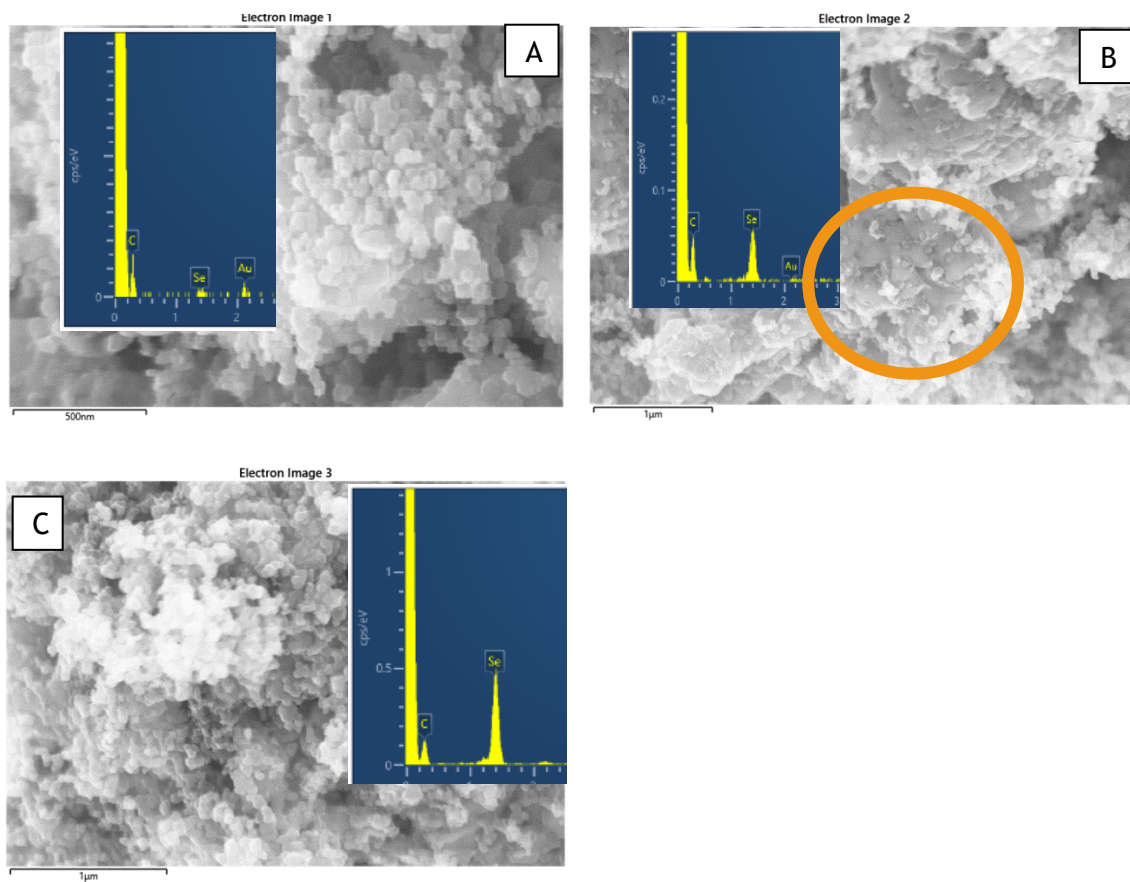


FIGURE 11 CB-6(1:2) SEM AND EDX SITE 1 (A), SITE 2 (B), SITE 3 (C)

-CB-6(1: 3)

The two sites analyzed (FIGURE 12) showed an important amount of Se in the EDX since the peak referred to the selenium has a particularly high intensity. Once again, all the images don't show the presence of smooth surfaces that can be related to the presence of Se chunks that have not been encapsulated during the vacuum annealing reaction. It is possible to conclude that the Se detected with the EDX is all correctly encapsulated within the matrix.

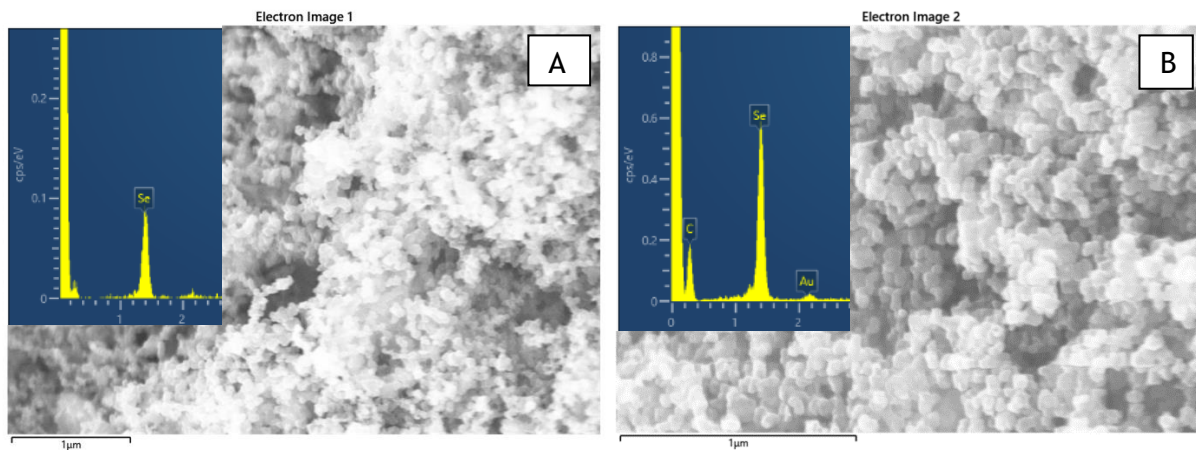


FIGURE 12 CB-6(1:3) SEM AND EDX SITE 1 (A), SITE 2 (B)

-CB-6(1:4)

FIGURE 13 showed the presence of Se inside all the sites of the sample considered in the EDX. However, no presence of selenium or smooth surface that can be related to it, were detected into the SEM images of the relative sites. It is possible to conclude that the encapsulation was successful and the Se has been encapsulated into the matrix.

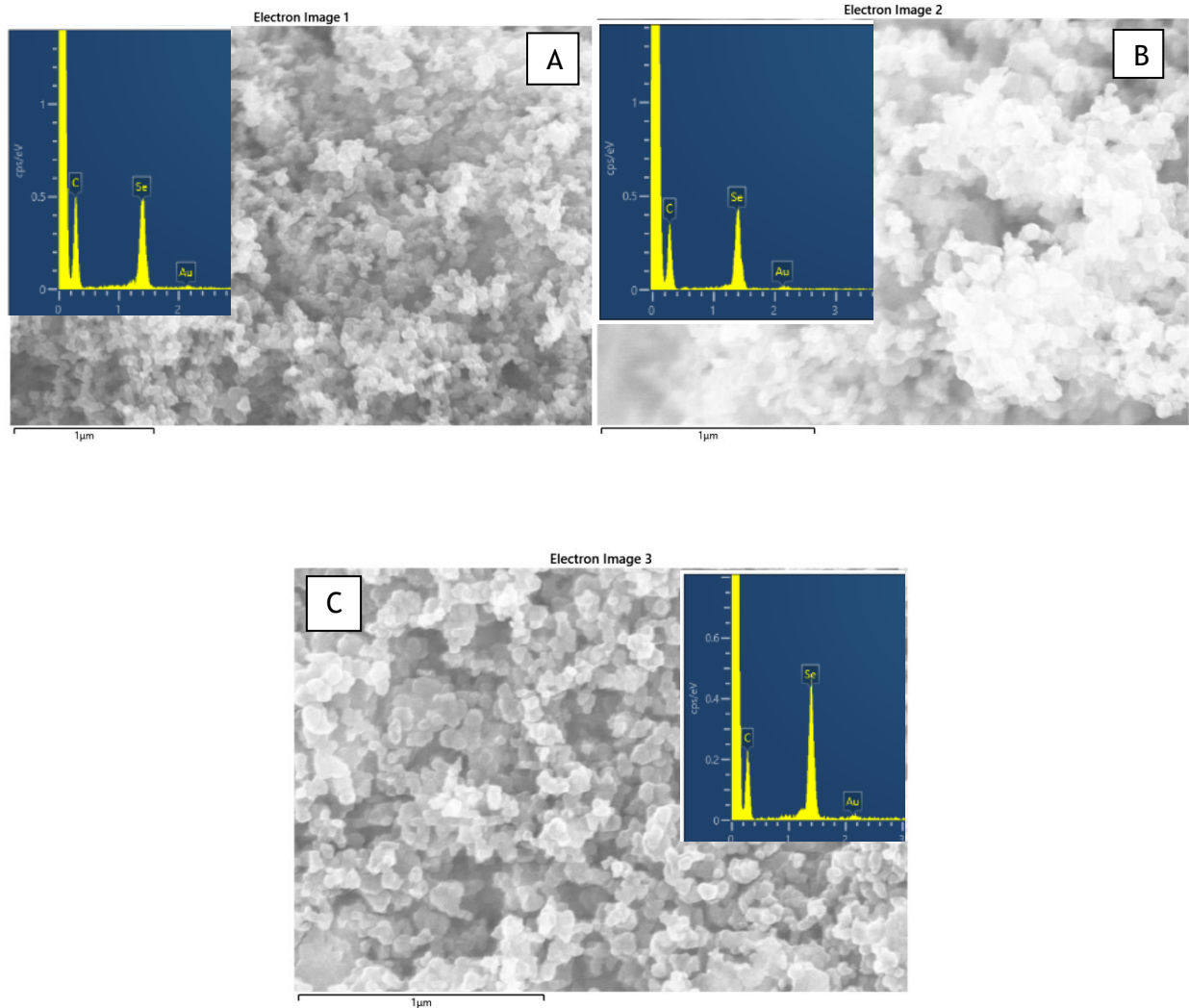


FIGURE 13 CB-6(1:4) SEM AND EDX SITE 1 (A), SITE 2 (B), SITE 3 (C)

-CB-6(1:6)

It is possible to notice that in the sample CB-6(1:6) (FIGURE 14) many chunks of Se are present, in FIGURE 14A it is circled a possible chunk of selenium. Indeed, the porous surface that should characterize the sample in that particular point seems to be too smooth to be part of the carbon matrix.

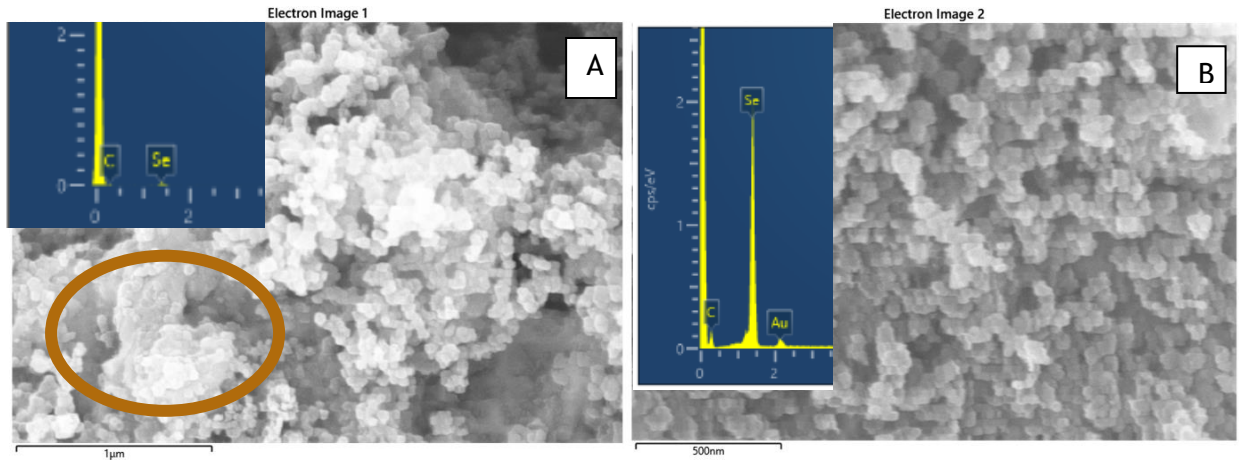


FIGURE 14 CB-6(1:6) SEM AND EDX SITE 1 (A), SITE 2 (B)

In conclusion, it is possible to define that the matrix showed the best results and the major amount of selenium encapsulated in the sample CB-6(1:4); samples CB-6(1:1) and CB-6(1:3) showed good encapsulation since in the sample there were no presence of visible selenium chunks; indeed, in CB-6(1:2) and CB-6(1:6) two chunks of se were detected, meaning the encapsulation process with this ratio did not undergo correctly and the selenium, instead of being inside the matrix were found outside. Consequently the ratio 1:4 was selected for proceeding with the experiment.

Once defined an optimal ratio, all the matrixes have been encapsulated using it and SEM and EDX have been carried out to define the differences between the 6 samples.

This analysis aimed to find all the visual differences between the samples considered and to hypothesize if the encapsulation reaction worked successfully. In particular, the SEM could visually find if there were selenium non encapsulated and the EDX was used to define the presence of all the elements inside the samples analyzed.

In FIGURE 15 the SEM and the EDX of some sample sites are showed. All the samples from CB-1 to CB-5 showed a poor encapsulation. Furthermore, large presence of Se chunks (FIGURE 15A and 15B), have been detected in samples CB-1 and CB-2. Analyzing the sample CB-5 it did not show any visual presence of se chunks inside it, however it showed very low peaks of Se to the EDX (FIGURE 15C). Hence, it may be related to an issue during the encapsulation process; the selenium could have vaporized and instead of undergoing an encapsulation reaction it could have deposited onto the surface of the glass tube used. However, CB-6 showed a low presence of Se chunks and the area without evident chunks showed the presence of Se to the EDX, meaning the encapsulation was successful and the selenium is expected to be inside the matrix (FIGURE 15D).

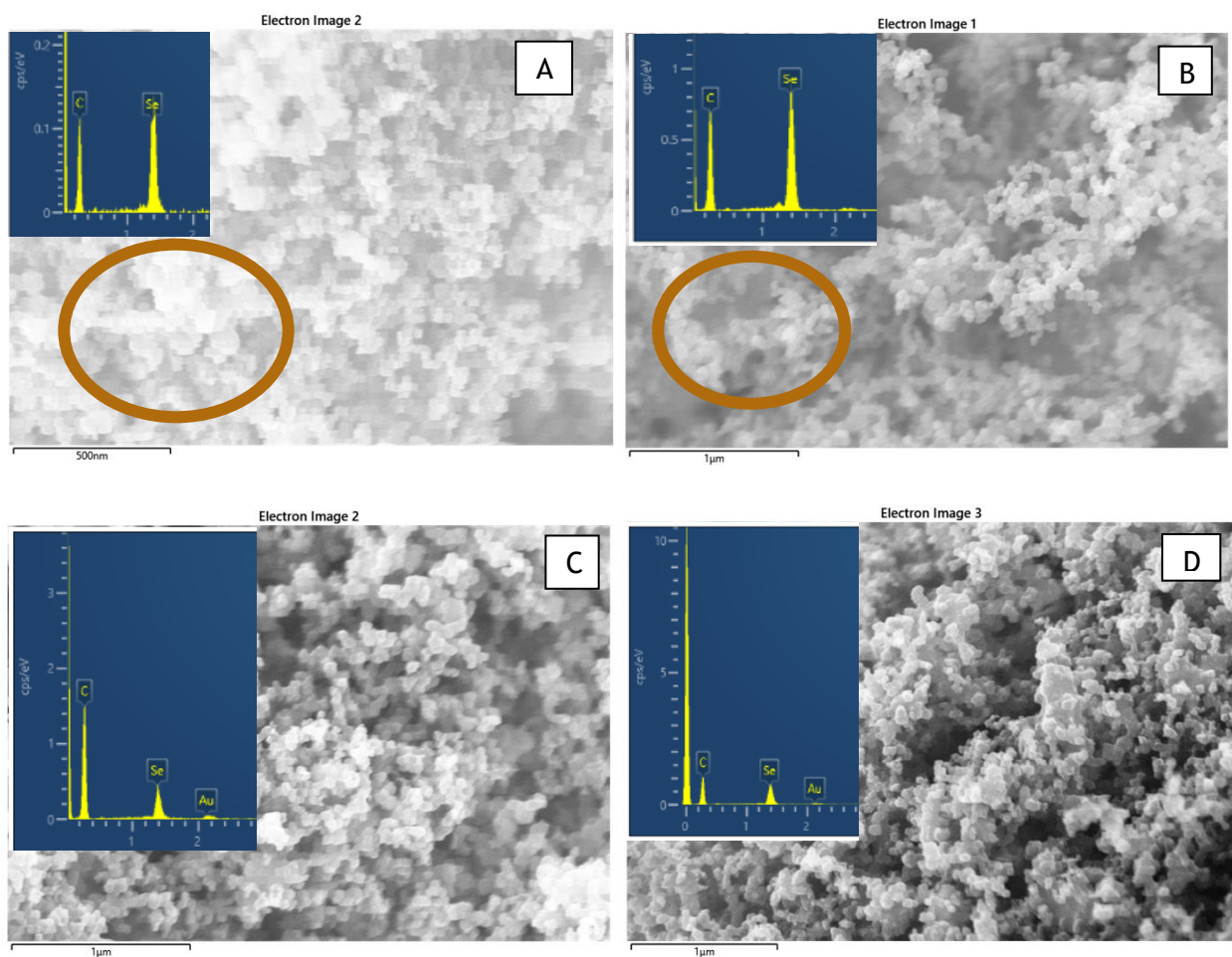


FIGURE 15 SEM AND EDX OF CB-1 (A), CB-2 (B), CB-5 (C) AND CB-6 (D) ENCAPSULATED WITH RATIO 1:4

TGA

In Fig. 16 the TGA of CB-1 (FIGURE 16A) and CB-5 (FIGURE 16B) are illustrated. It seems there is around 60% Se mass loading in both composites (because ~40% mass remained after heating up), and CB-5 seems to have a slightly higher Se loading than CB-1, which could indicate that a higher level of defectivity in the matrix might be beneficial to load a higher amount of Se. Compared to previous work, the amount of Se is slightly less. Indeed, most of the encapsulation techniques achieved a Se mass percentage of 50 - 52%.

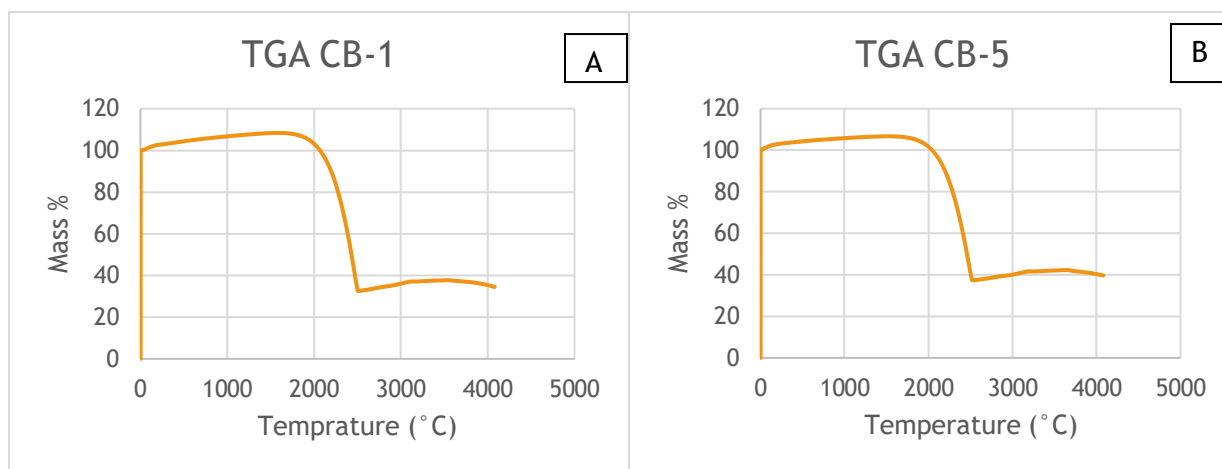


FIGURE 16 TGA CB-1 (A), CB-5 (B)

Taking in consideration the results of the analyses, it is possible to notice that the sample that showed less selenium chunks had also a slightly higher percentage in mass of selenium loading meaning probably that, the higher amount of peroxide added, had favored the encapsulation process.

Concluding, all the samples showed different defectivity at an atomic level and no samples showed a reconstruction of the surface given to an undesired polymeric reaction. The different amount of peroxide not only affected the different defectivity, but they also may have affected the different size of the pores present in the matrix. Indeed, the different amount of selenium inside the samples showed in the TGA could be possible only with larger pores. Hence, it may be hypothesized that

a higher number of mesopores over micropores may be found in samples with higher concentration of peroxide and, it brings to an enhanced quantity of selenium encapsulated.

ELECTROCHEMICAL RESULTS

CB-1 and CB-5 were chosen to define the differences between the two matrixes with the lowest and the highest amount of added peroxide.

The storage performance was tested using galvanostatic charge/discharge (GCD). Existing studies have shown that an appropriate voltage range was 0.5-3 V. The CB electrodes were used as the cathode in the half-cell. Thus, K^+ reaction with Se is represented by the discharge/charge processes. The electrodes were discharged and charged at 50 mA g^{-1} for 100 cycles. The samples chosen were CB-1 and CB-5.

Both CB-5 (FIGURE 17B) and CB-1 (FIGURE 17A), electrode showed a very low capacity after the first cycle, 150 /g^{-1} (point 1 Fig. 16 B) and 80 mAh/g^{-1} (point 1 Fig. 16 A) and it subsequently dropped quickly, respectively 18 mAh/g^{-1} (point 2 Fig. 16 B) and 55 mAh/g^{-1} (point 2 Fig. 16 A) . The reason because the first cycle has a higher capacity may be attributed to the SEI layer. The SEI layer is important in maintaining the stability of the electrode and the cycling ability as the SEI layer prevents the decomposition of the electrolyte by blocking the diffusion of electrons to the electrolyte.

The reason the first cycle capacity is low may be attributed to the concentration of the electrolyte. Thus, the same samples were chosen to be analyzed with KFSI in DME 7M. Previous experiments showed that a higher concentration of electrolyte in K-Se batteries may improve the performances and give the battery a higher capacity.

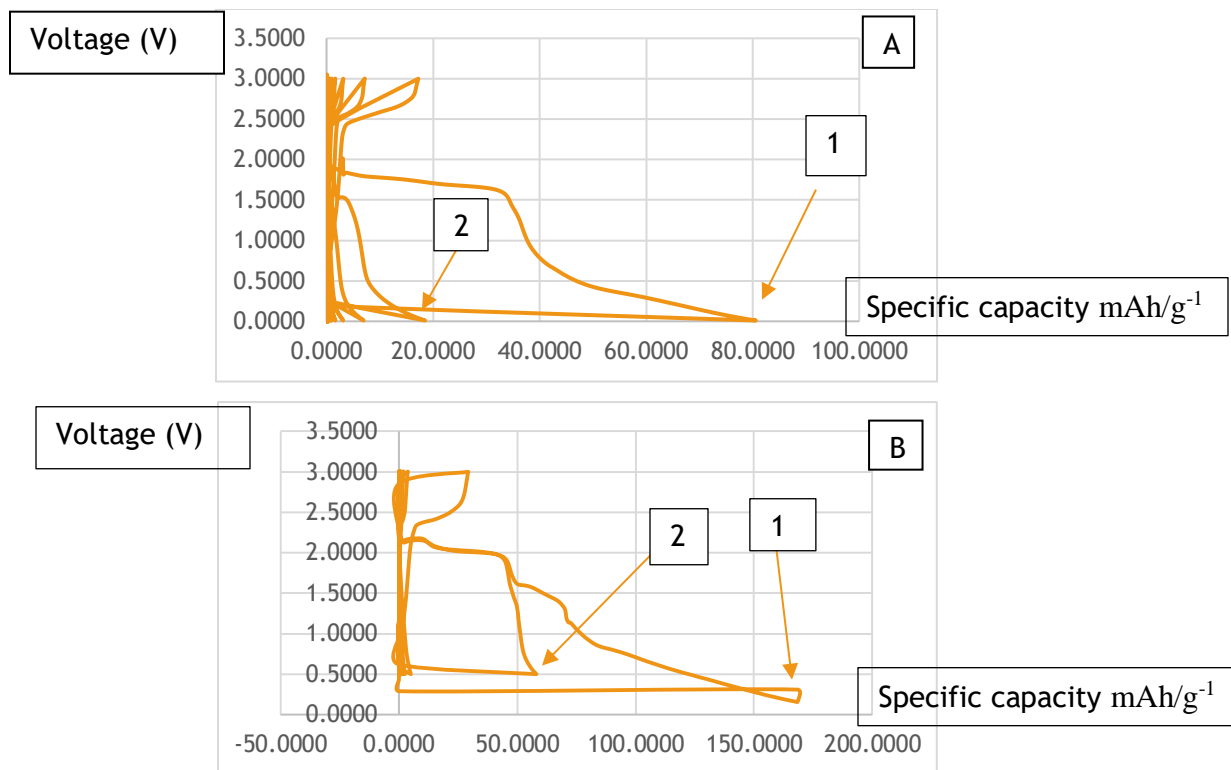


FIGURE 17 GALVANOSTATIC CHARGE/DISCHARGE PROFILE CB-1 (A), CB-5 (B) USING KFSI EDC/ED 1M

After changing the concentration of electrolyte, GCD was carried out again and some improvements were seen (Fig. 18). The initial capacity increased, moving from 80 mAh/g⁻¹ to 320 mAh/g⁻¹ (point 1 Fig. 18 A) for CB-1 and from 150 mAh/g⁻¹ to 350 mAh/g⁻¹ (point 1 Fig. 18 B) for CB-5. Probably, by improving the concentration of the K⁺ ions in solution, more K⁺ ions could reach the cathode and subsequently undergo the reaction. In the graphs it is possible to see a single plateau in the first discharge curve. This is referred to the reaction of K ions with the selenium and it proves the reaction occurred as expected. In Fig. 18 more than one plateau is observed, it can be explained referring to the formation of K₂Se_n composites. Indeed, the potassium first product in this reaction is K₂Se₆ and then it turns into K₂Se. The trend of the curves obtained corresponded to the ones present in literature. It has been demonstrated in previous experiments that the reaction that takes part in this battery involves the formation of K₂Se_n (n=2-6), and for every different composite it may be possible to have a different plateau.

However, even though the initial capacity was improved, after the first cycle the capacity dropped suddenly as seen in the cycling performance graph (Fig. 17 and Fig. 18).

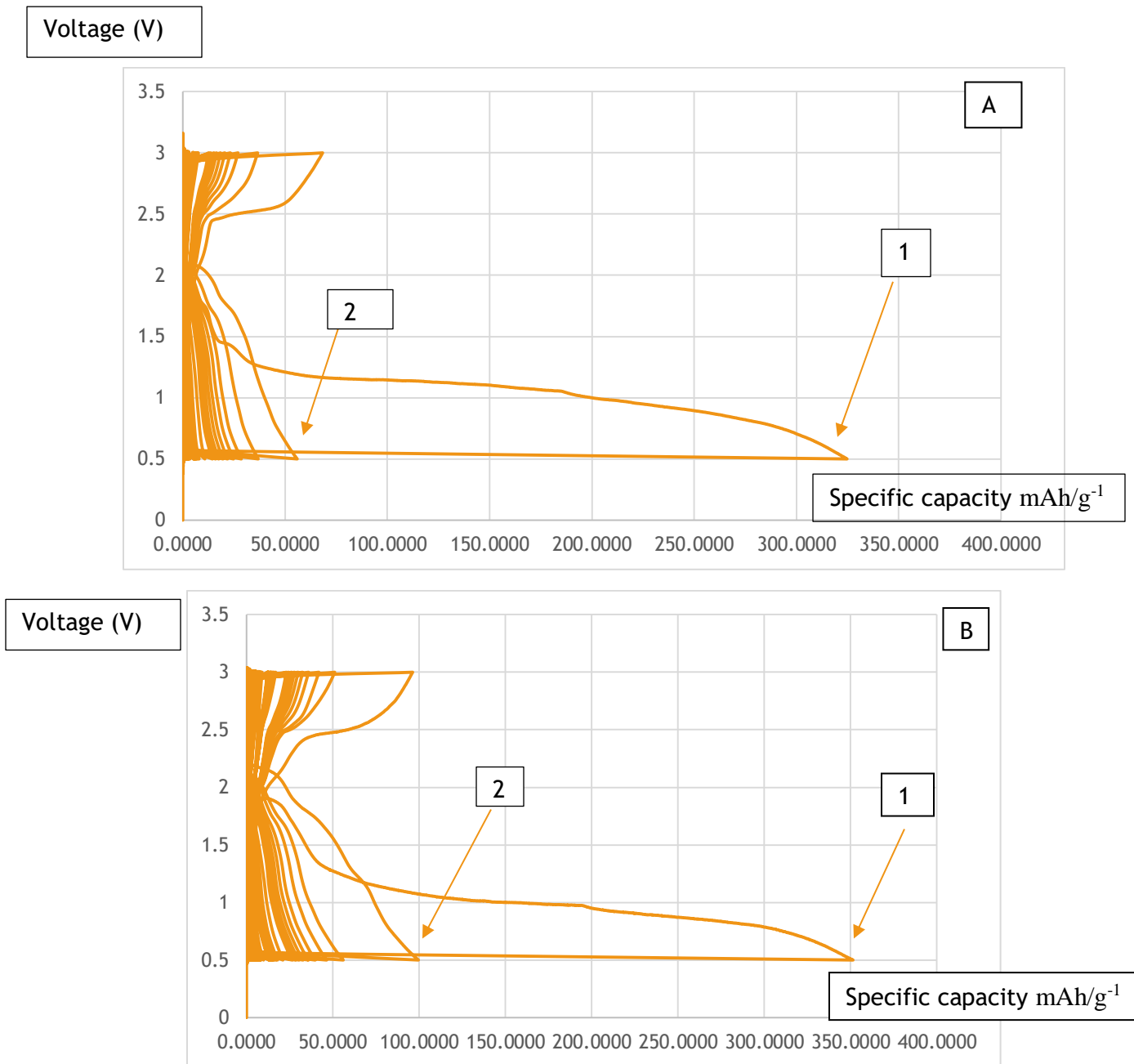


FIGURE 18 GALVANOSTATIC CHARGE/DISCHARGE PROFILE CB-1 (A), CB-5 (B) USING KFSI IN DME 7M

The line in Fig. 19 and Fig. 20 describes the specific capacity referred to the discharge process. After the first cycle all the batteries showed an important drop of capacity. It may be referred to the dissolution of the polyselenides into the electrolyte and so to the shuttle effect. To prove it a coin cell battery has been made using Se non encapsulated in any carbon matrix and the outcomes were analyzed and discussed.

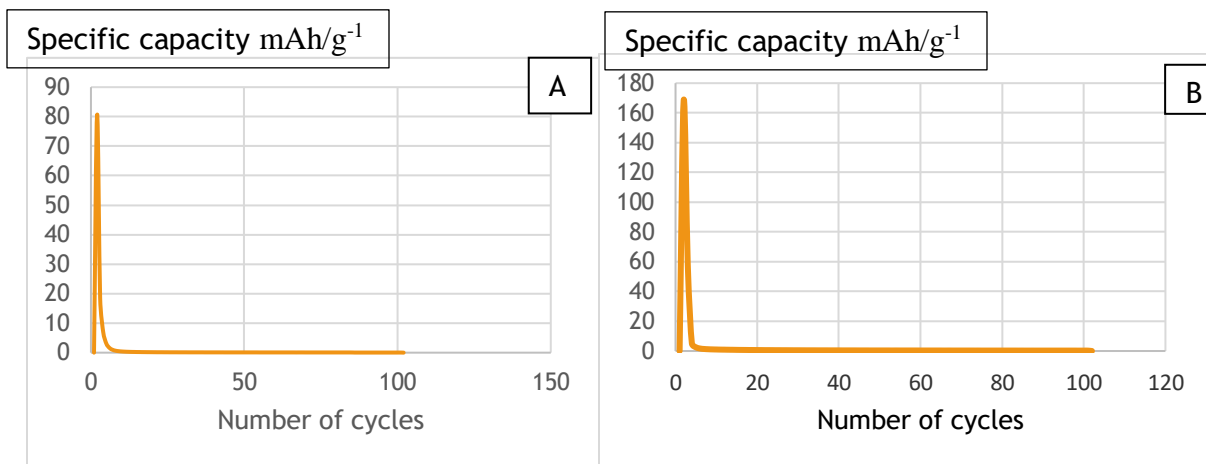


FIGURE 19 CYCLING PERFORMANCE OF CB-1 (A) AND CB-5 (B) KFSI 1M

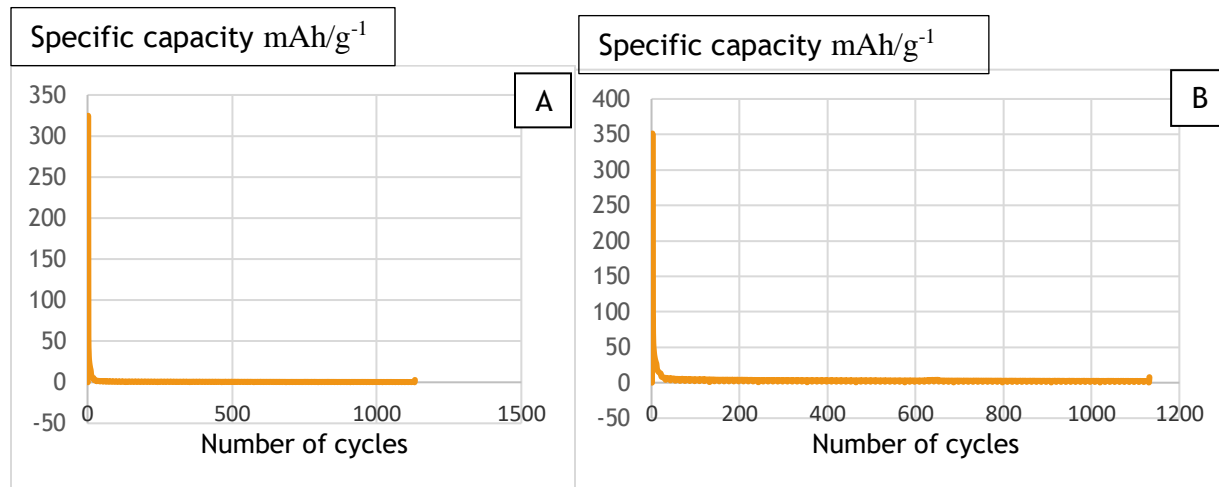


FIGURE 20 CYCLING PERFORMANCE OF CB-1 (A) AND CB-5 (B) KFSI IN DME 7M

The results (Fig. 21) showed a similar trend of the other samples analyzed. The capacity, after the first cycle where it is high, dropped suddenly in the next few cycles. Since the K-Se with potassium not encapsulated in any matrix shows an important shuttle effect that leads to a drop of capacity, it can be hypothesized that also the batteries with the samples CB-1 and CB-5 suffers of this issue.

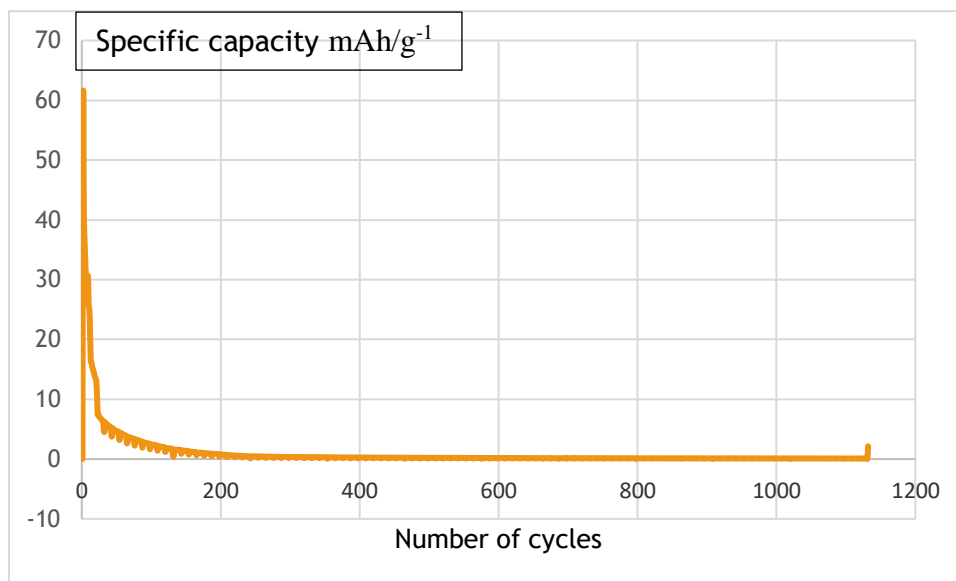


FIGURE 21 CYCLING PERFORMANCE OF K-SE BATTERY IN KFS IN DME 7M

It is possible to conclude that the polyselenides dissolved into the electrolyte, both in CB-1 and CB-5.

In literature are present many different matrix and ways to encapsulate Se for K-Se batteries. Some of them showed a better initial capacity and therefore, a more stable capacity that lasted for at least 100 cycles.

For instance, Yajie Liu et al build a Se cathode encapsulating this material into a PAN carbon nano matrix. They obtained an initial capacity of 625 mAh/g⁻¹ and it lasted stable around 356 mAh/g⁻¹ for the next 100 cycles. In their work the origin of the superior electro-chemical behavior is probably the confinement of small molecule Se in the PAN-derived carbon matrix, which could

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inhibit the formation of polyselenides and avoid their dissolution. Meanwhile, the conductive carbon matrix could also successfully deal with problems such as the large volume changes and low conductivity of selenium [11].

Xianglong Huang et al used a porous carbon matrix to encapsulate Se; the results of the TGA showed a loading of Se of 53% and the GCD outcomes gave an initial capacity of 340 mAh/g⁻¹ and it stays stable around 216 mAh/g⁻¹ in the next 100 cycles. In their work the porous structure provides enough storage space to accommodate selenium and the good electronic conductivity of carbon matrix guarantees the good electrochemistry performance [12].

5 Conclusion

The work aimed to explore and optimize an encapsulation technique for Se; it was tried to be encapsulated in a porous carbon matrix using a vacuum annealing technique. The encapsulation showed the best results when high amounts of peroxide were added (CB-5). Previous experiments demonstrated that high concentration of peroxide may lead to reconstructions and subsequently it may create more space for the molecule of Se to encapsulate into the matrix. Indeed, small amount (CB-1/2/3/4) of peroxide creates atomic level defects, which may create an insufficient big porosity for the selenium to get into the matrix and therefore be encapsulated.

Using the samples as a cathode for a battery showed poor electrochemical performances and the issue of the dissolution of the polyselenides could not be avoided. The capacity dropped after the first cycle, and it was proven that the performances with the Se encapsulated were similar to a non encapsulated Se cathode. It may be possible to suppose that most of the Se present did not benefit from the encapsulation. The big pores made with a high amount of peroxide made it possible to accommodate a higher amount of Se however, their presence may have given the chance to the K_2Se_n compounds to freely dissolve into the electrolyte. Furthermore, it has been demonstrated in previous works that the micropores can effectively restrict the dissolution of polyselenides owing to volume constrains and the mesoporous with small pores accommodates the selenium and restricts the dissolution of polyselenides, while mesoporous with larger pores can enhance the amount of selenium that can be accommodated so the electrolyte can infiltrate more efficiently.

Confronting the outcomes obtained with the ones present in literature, the encapsulation for the selenium was successful at high concentration of peroxide while in past experiments the same matrix, used to encapsulate sulfur, showed great results and good encapsulation proprieties with small concentration of peroxide matrixes.

In future projects, it will be necessary to further optimize the encapsulation of the Se. It could be worth to change the temperature of the encapsulation reaction. Since the boiling point of Se is

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685°C, it may be worth to try to increase the encapsulation temperature in the furnace to see if there are any changes within the amount of Se encapsulated. The Se will be more volatile at higher temperatures and so it may get into the matrix more easily. Also, it may be interesting to understand what happens when Se is encapsulated in matrixes with higher concentrations of peroxide, such as 15ml or 20ml. Since the best encapsulation results were showed in the CB-5 sample it will be useful to keep increasing the amount of peroxide in order to make further changes into the carbon; it may create even more space for the Se to be hosted into the carbon porous.

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