Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
This journal is © The Royal Society of Chemistry 2018

Supplementary Information

Marcasite Iron Sulfide as a High-Capacity Electrode Material for Sodium Storage

Natalia Voronina[a], Hitoshi Yashiro[b], Seung Taek Myung[a,*]

[a] Department of Nano Technology and Advanced Materials Engineering, Sejong Battery Institute, Sejong University, Seoul, 05006, South Korea.
[b] Department of Chemistry and Bioengineering, Iwate University, 4-3-5 Ueda, Morioka, Iwate 020-8551, Japan

*Corresponding author

Tel: 82 23408-3454, fax: 82 23408-4342, e-mail: smyung@sejong.ac.kr (S.T. Myung)

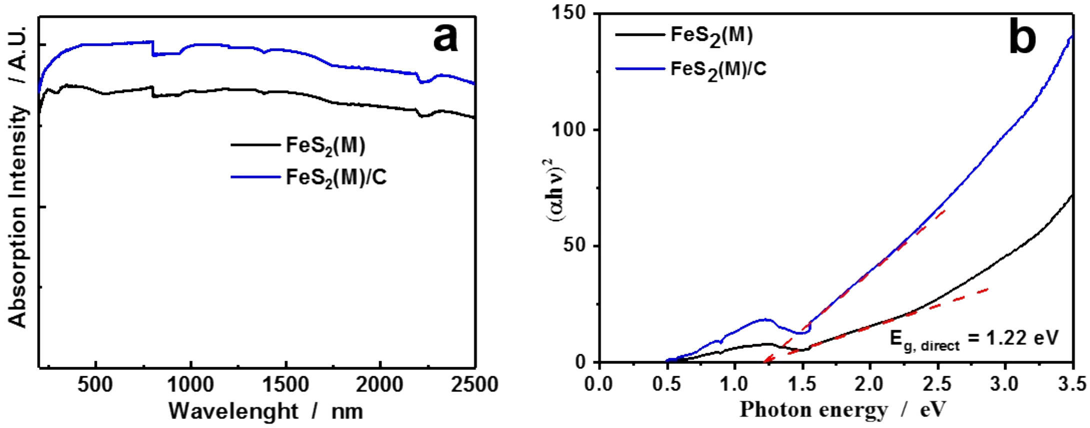
SI Table 1. Structural parameters obtained from Rietveld refinements for FeS_2(M) and FeS_2(M)/C

FeS_2(M)

Composition			FeS_2			
Space group			*Pnnm*			
Atom	Wyckoff Position	x	y	z	B / Å^2	g
Fe	2*a*	0	0	0	0.04	1
S	4*g*	0.202(5)	0.382(5)	0	0.05	1
Lattice parameters			a=4.447(5)Å b=5.427(5)Å c=3.387(5)Å			
R_p / %			6.82			
R_{wp} / %			9.08			

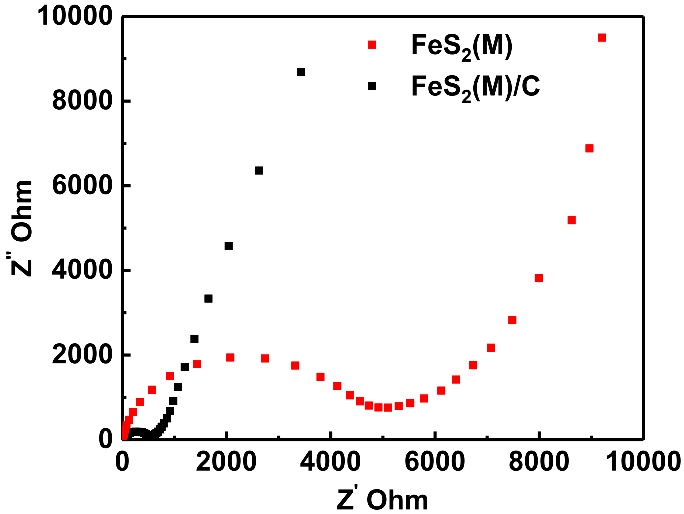
FeS_2(M)/C

Composition			FeS_2			
Space group			*Pnnm*			
Atom	Wyckoff Position	x	y	z	B / Å^2	g
Fe	2*a*	0	0	0	0.05	1
S	4*g*	0.202(5)	0.382(5)	0	0.06	1
Lattice parameters			a=4.447(5)Å b=5.427(5)Å c=3.387(5)Å			
R_p / %			5.14			
R_{wp} / %			6.37			

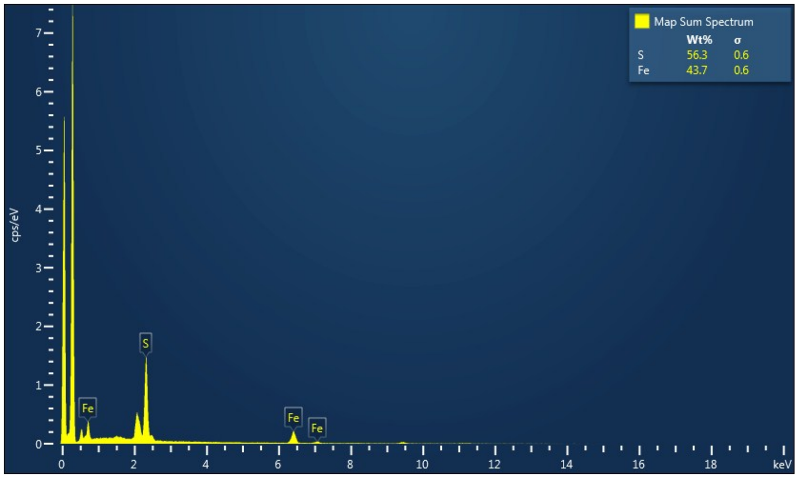


SI Figure 1. (a) UV-vis-NIR absorbance spectra of FeS_2(M) and FeS_2(M)/C (b) Tauc plots of FeS_2(M) and FeS_2(M)/C

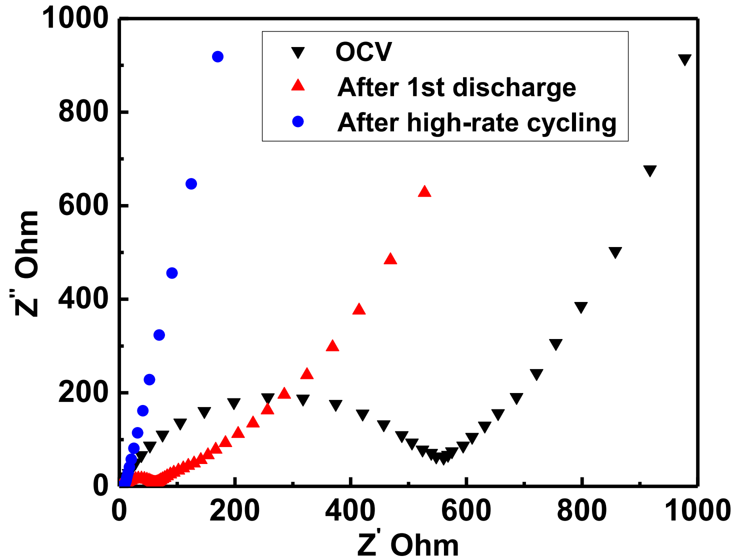
The optical behavior of FeS_2(M) and FeS_2(M)/C was studied by UV-vis-NIR absorbance spectroscopy. From the absorbance spectra, the optical band gaps of FeS_2(M) and FeS_2(M)/C were calculated by using Tauc equation.[1] The measurement showed a direct band gap of 1.22 eV with a subgap optical absorption at 0.5 eV for both FeS_2(M) and FeS_2(M)/C materials.



SI Figure 2. AC impedance spectra of FeS_2(M) and FeS_2(M)/C composite before cycling.

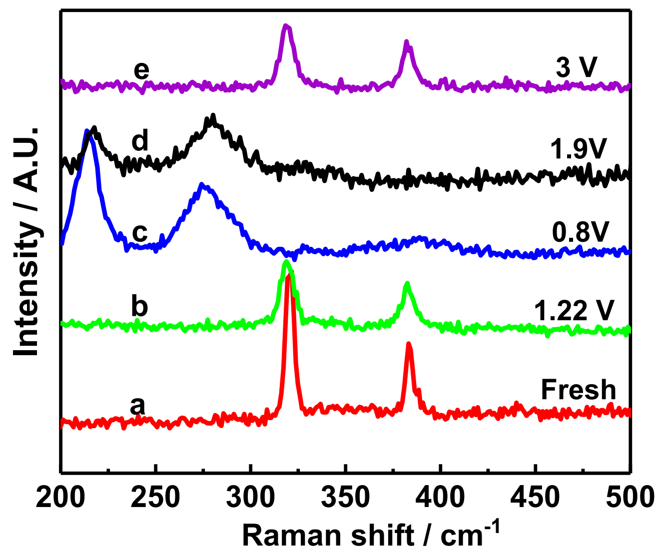


SI Figure 3. EDX spectrum of FeS_2(M).



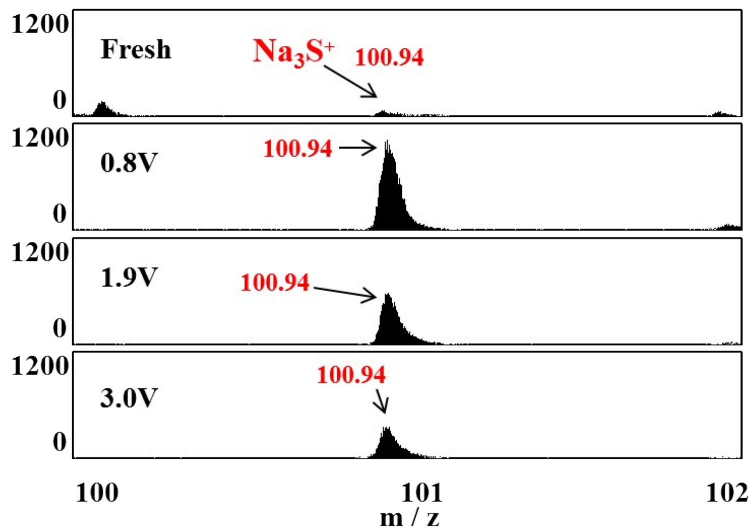
SI Figure 4. AC impedance spectra of FeS_2(M)/C before cycling OCV, after 1st discharge to 0.8V and after high-rate cycling.

Impedance Nyquist plots were collected before cycling at OCV, after first discharge and after high-rate cycling. The Nyquist plot shows that the charge transfer resistance decreases significantly after first discharge proceeds and even underwent significant reduction after charge-discharge cycles, especially after high-rate cycling, which prove that the superior rate capability is attributed to the improved charge transfer.



SI Figure 5. Raman spectra of FeS_2(M)/C electrode (a) fresh (b) discharged to 1.22 V (c) discharged to 0.8 V (d) charged to 1.9 V (e) charged to 3 V

Ex situ Raman was used to identify the structural transformations of FeS_2(M)/C composite during first discharge and charge. The Raman spectra of fresh electrode exhibit two peaks of A_g mode of FeS_2(M) structure. These peaks started to weaken as the sodiation goes and disappear at 0.8 V. At the same time three significant modes at 217, 274, 384 cm^{-1} ascribed to FeS structure[2] appeared and observed at discharge to 0.8V. During further desodiation, the peaks of FeS structure start to decrease and at the end of charge A_g vibration of FeS_2(M) reforms back, indicating that the reaction of FeS_2(M)/C composite is highly reversible.



SI Figure 6. TOF-SIMS spectra of FeS_2(M)/C upon sodiation (discharge) to 0.8 V and desodiation (charge) to 3 V, Na_3S^+ positive fragment (m=100.94)

References

1 J. Tauc, A. Menth, *J Non-Cryst Solids*, 1972, **8–10**, 569–585

2 P.Ramakrishnan, S. Shanmugam, J. H. Kim, *ChemSusChem*., 2017, **10**, 1 – 10