Elucidating the Role of Sulphur in Cycling Reversibility of CVD Sulphur Doped Porous Hard Carbon Anodes in Sodium Ion Batteries

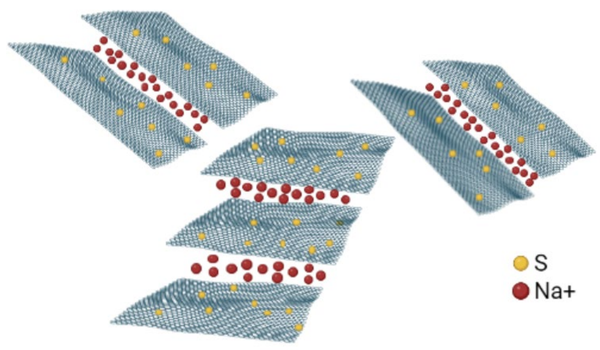
Sarat Alabidun[1], Luke Chater[2], Matthew T. Darby[2], Federico Raffone[2], Paolo Restuccia[2], Yuming Sun[2],Heather Au[1], Clotilde S. Cucinotta [2§], Carla de Tomas[1‡], Maria Crespo-Ribadenyra[1‡] and Maria-Magdalena Titirici[1‡]

[1]Imperial College London Department of Chemical Engineering, Exhibition rd South Kensington. SW7 2AZ

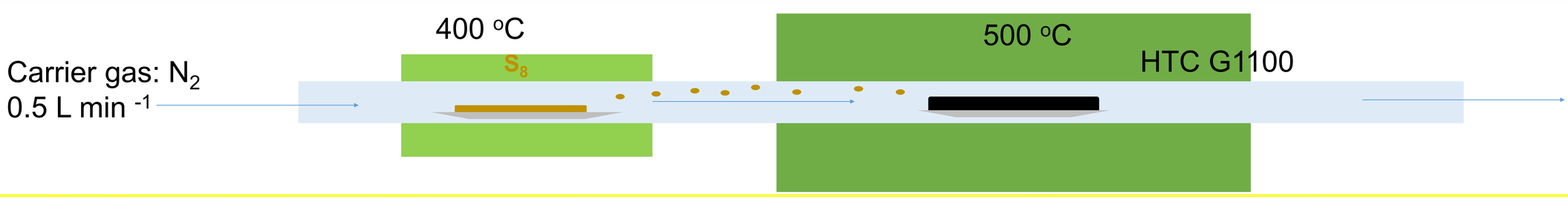
[2]Imperial College London Department of Chemistry, White City Campus, 10 wood In White City W12 7TA

MOTIVATION

- Hard carbon anodes in sodium ion batteries experience high initial capacity loss/poor coulombic efficiency and irreversibility
- Heteroatoms including sulfur, nitrogen and phosphorus have been used to enhance the anode electrochemical performance and reduce irreversibility, however their role in on the electrochemical performance are not completely understood, while many of the current doping methods are complex
- This work- Introduces a facile method of sulfur doping, elucidates the role of sulphur in enhanced electrochemical performance of Hard Carbon anodes using computational and experimental methods



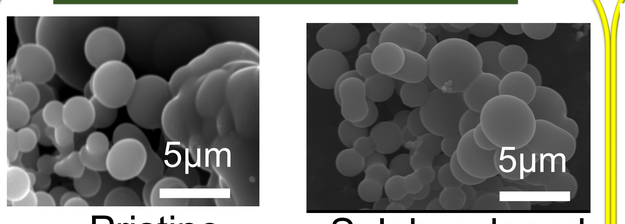
HARD CARBON DOPING



RESULTS

Materials & Electrochemical Characterisation

SEM & Elemental Analysis

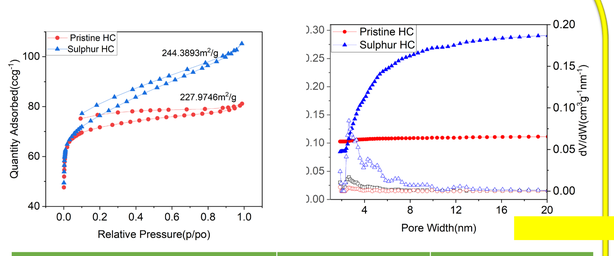


Pristine Sulphur doped

Name	N [%]	C [%]	H [%]	S [%]
Pristine HC	0.11	84.97	1.29	0.06
Sulfur HC	0.11	80.00	1.38	3.15

SEM shows similar structure , while elemental analysis indicates ~ 3% sulphur doped

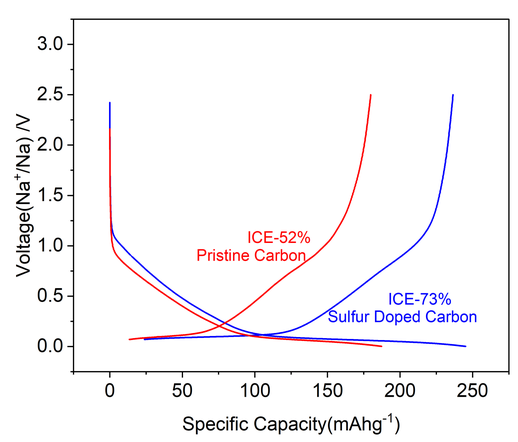
BET and Raman



	D:G Ratio	G band Shift
Pristine HC	0.99	1596
Sulfur HC	1.02	1590

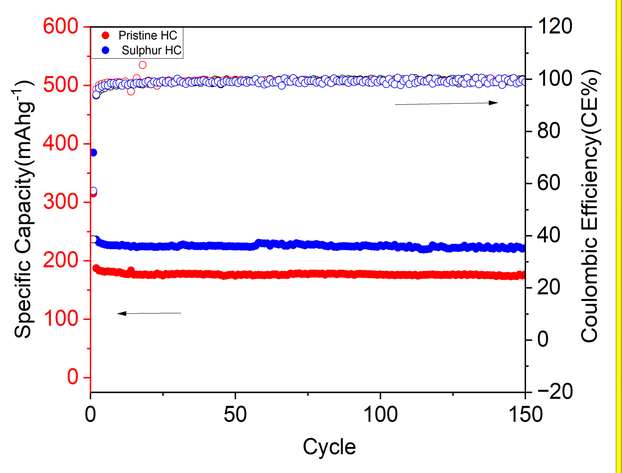
- Larger mesopores in doped indicate possible higher sodium storage capacity
- Increased D:G ratio shows presence of more defects

Voltage Profiles



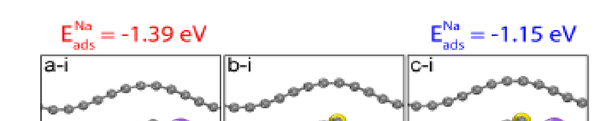
Increased reversible capacity and plateau capacity with sulphur doping. Confirming the increase in sodium storage in the larger mesopores

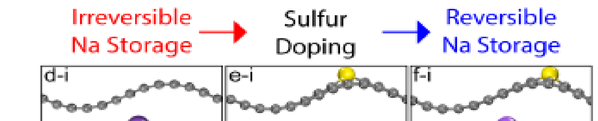
Electrochemical Characterisation



Stable cycle with higher capacity all through with sulphur doping

Modelling





- Sulphur is adsorbed in HC free edges; which allows strong adsorption of Na
- Na shows weaker adsorption in the presence of sulphur
- After relaxation Na moves and bonds strongly with C

CONCLUSION

In addition to increasing interlayer spacing or pore size to allow for better Na storage, sulphur helps to improve reversibility of hard carbon anodes in SIBs, due to its adsorption at the defects and its weaker binding energy with Na

ACKNOWLEDGEMENT

We would like to acknowledge the Damian Cummins scholarship, for providing PhD funding.

REFERENCES

1. Au H, Alptekin H, Jensen ACS, Olsson E, O'Keefe CA, Smith T, et al. A revised mechanistic model for sodium insertion in hard carbons. Energy & Environmental Science. 2020;13(10):3469-79.
2. Li Z, Bommier C, Chong ZS, Jian Z, Surta TW, Wang X, et al. Mechanism of Na-ion storage in hard carbon anodes revealed by heteroatom doping. Advanced Energy Materials. 2017;7(18):1602894.
3. Li W, Zhou M, Li H, Wang K, Cheng S, Jiang K. A high performance sulfur-doped disordered carbon anode for sodium ion batteries. Energy & Environmental Science. 2015;8(10):2916-21.