Carbon NANOstructures Laboratory

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Graphene-based electrodes for high-performance Na-ion batteries

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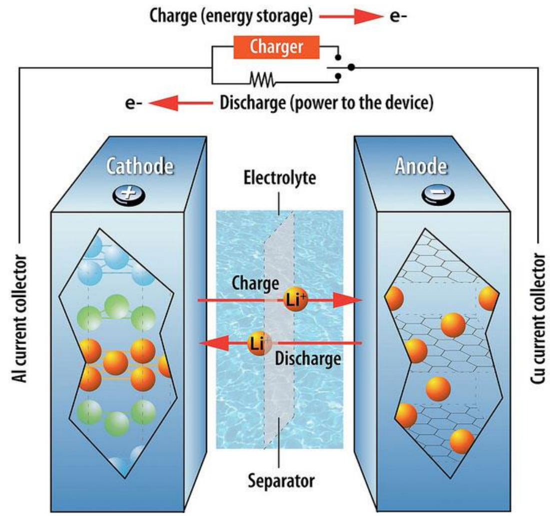
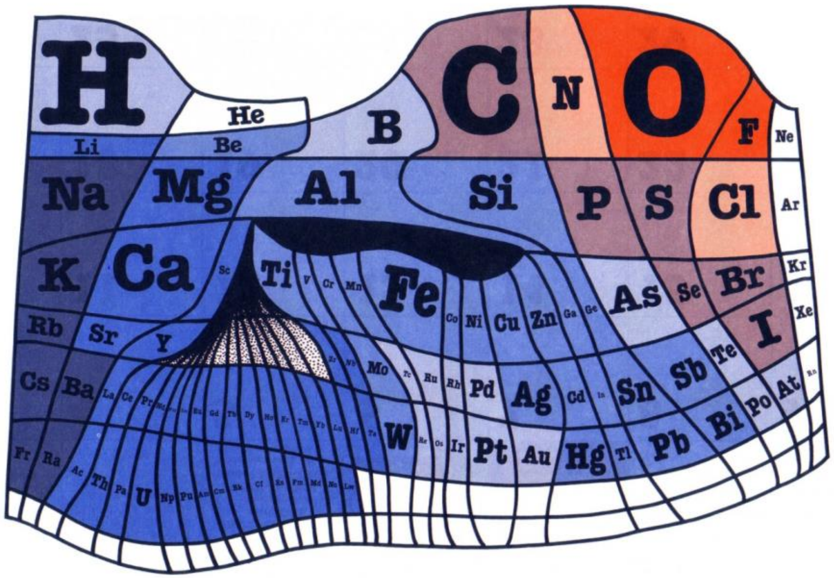
The Energy Revolution

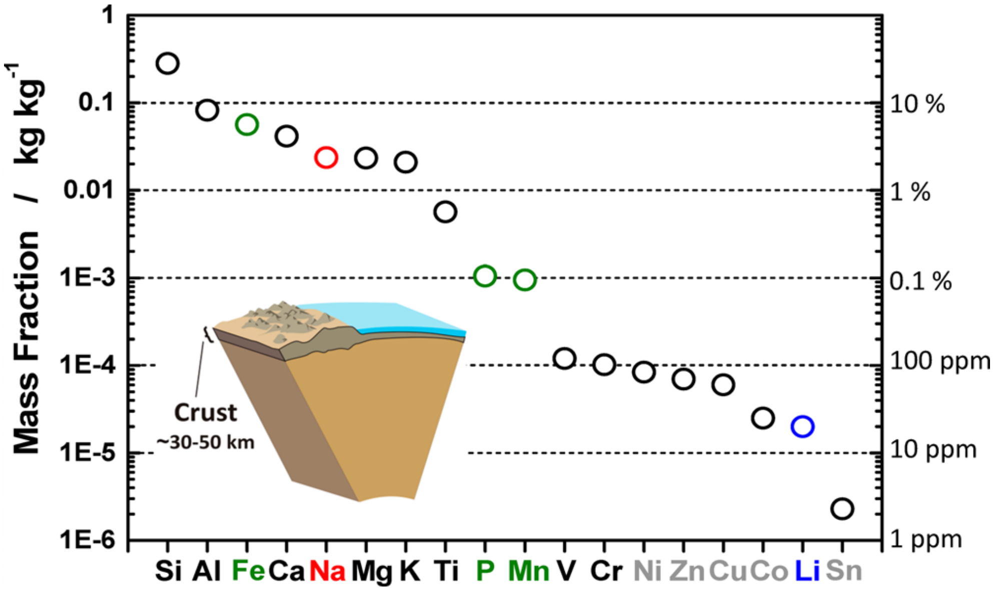


Smart grids

Automotive

Some drawbacks in Li-ion technology





Na+

Mg2+

Al3+

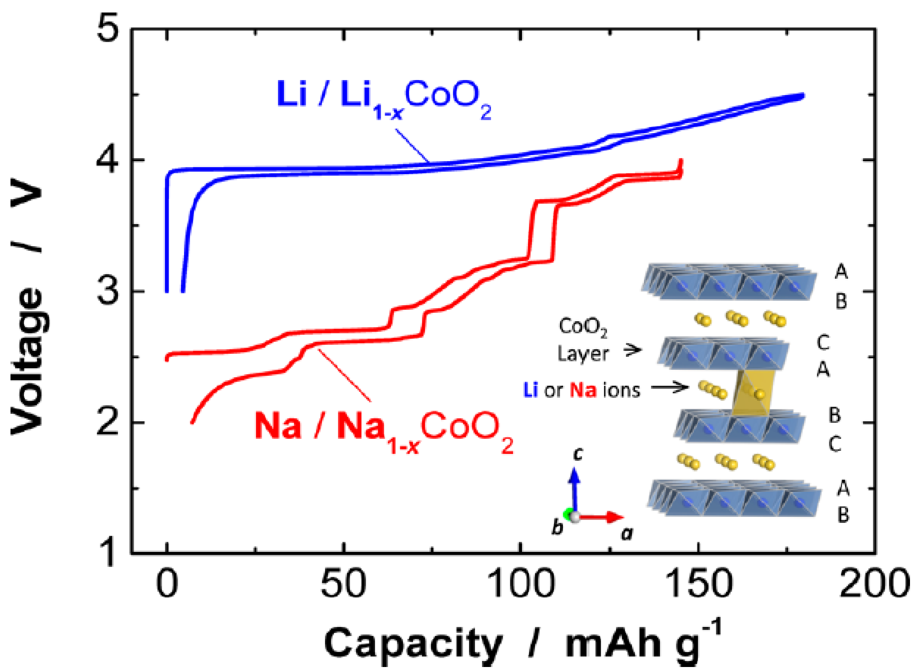
N. Yabuuchi, K. Kubota et al., Chem. Rev. 114, 11636 (2014)

Na-ion batteries

Na-ion batteries (SIBs) are promising for automotive and large scale grid storage applications

Advantages

- ✓ Na is more available in nature and less expensive than Li
- ✓ Li-ion technology can be partly recovered to assure rapid progress

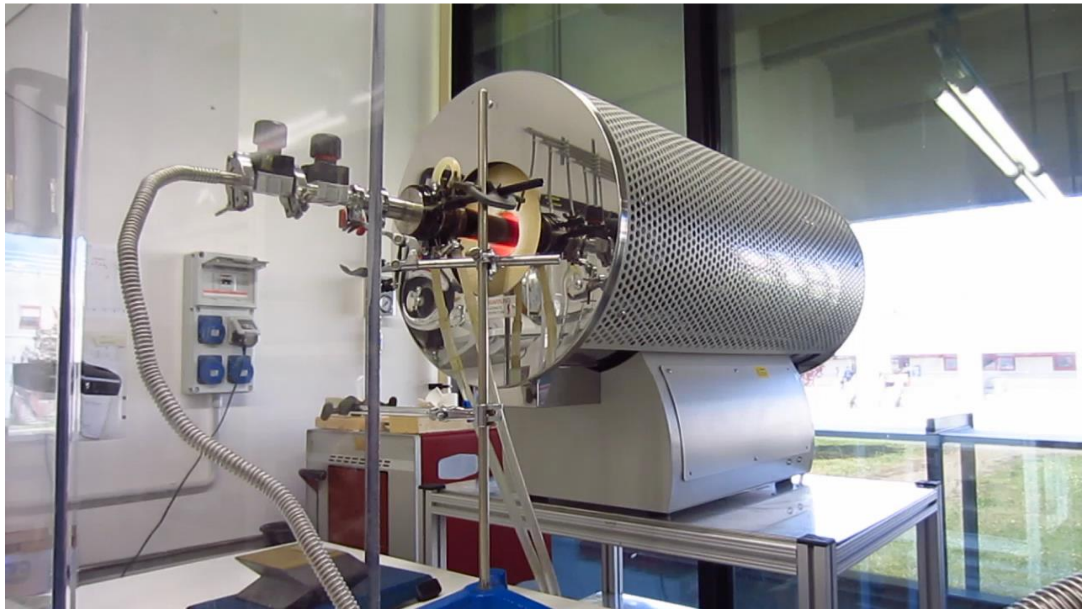


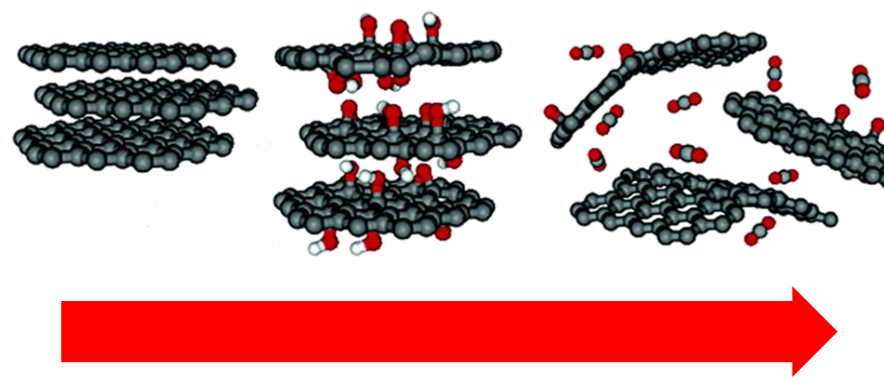
Disadvantages

- ✓ Na+ ionic radius is larger than Li+
- ✓ Na does not intercalate in graphite and silicon, commonly used in Li systems

But…

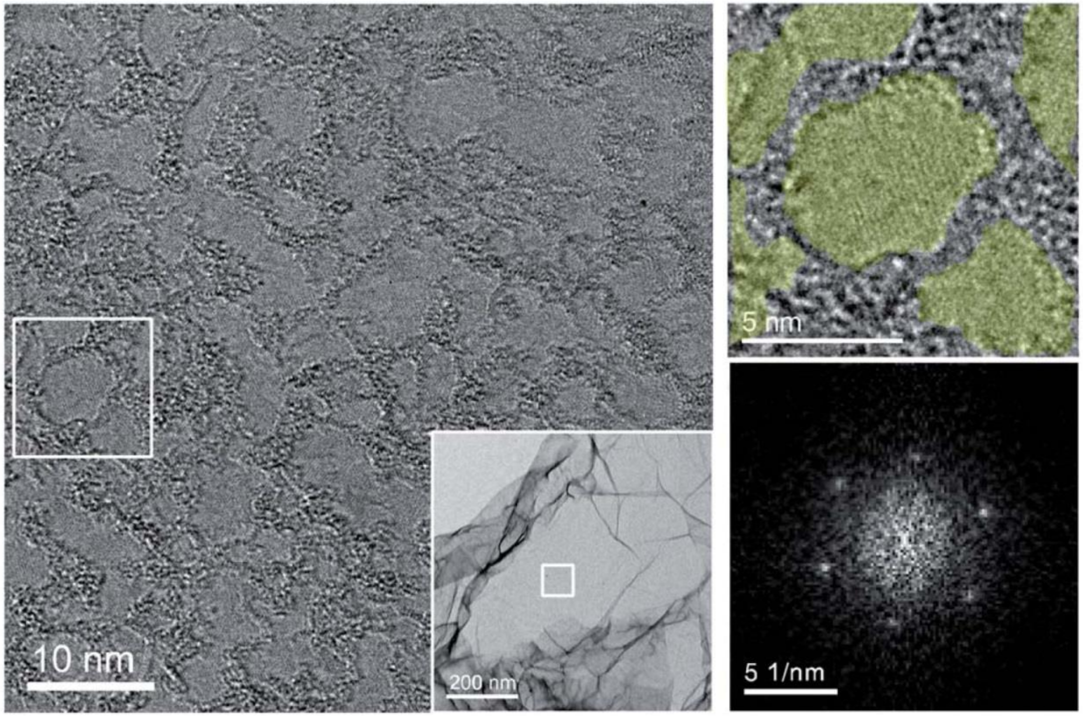
Graphene (TEGO) production

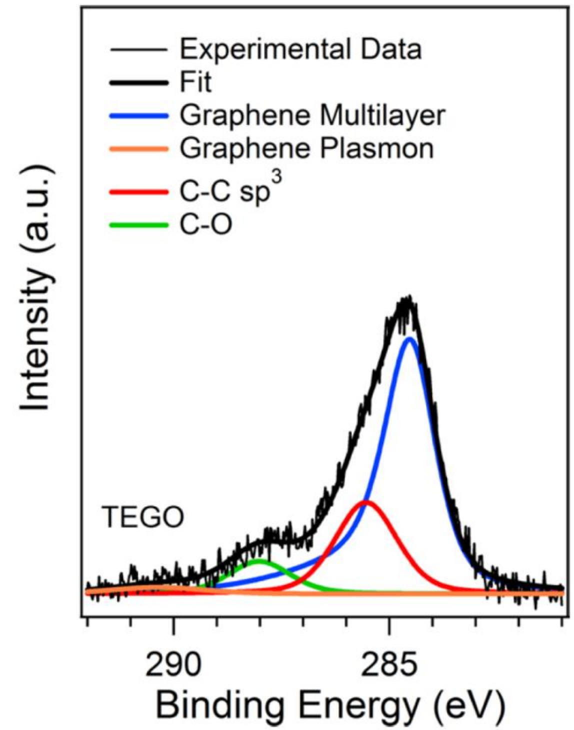


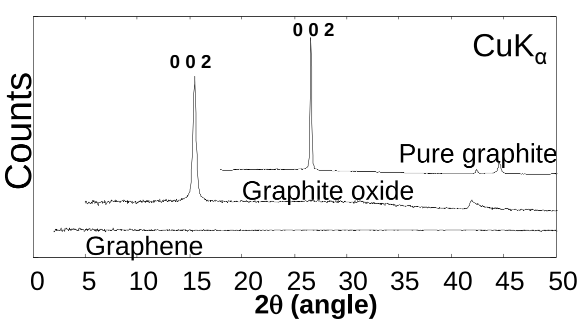


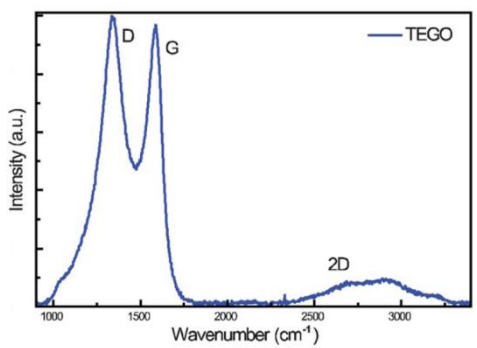
M. Riccò, D. Pontiroli , J. A. Stride et al, Nano Lett. 11, 4919 (2011)

TEGO Characterisation









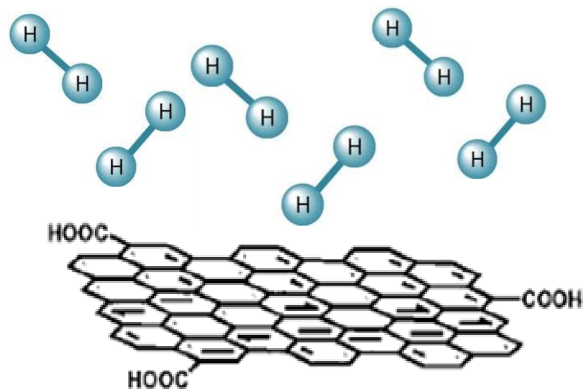
D. Pontiroli , M. Riccò et al., J. Phys. Chem. C 118, 7110 (2014)

M. Gaboardi, D. Pontiroli et al, J. Mater. Chem. A 2, 1039 (2014)

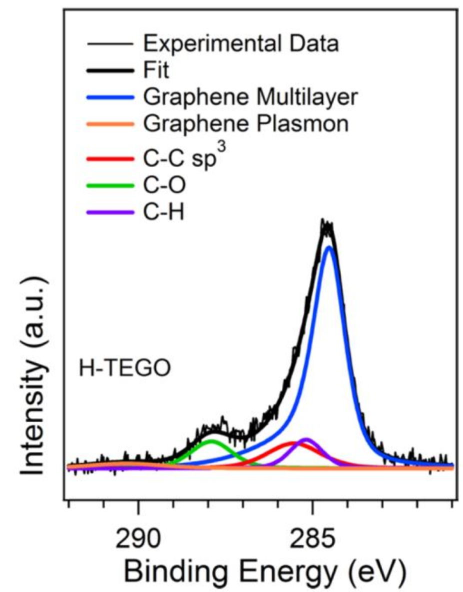
- ✓ Single and few-layers graphene sheets
- ✓ High specific surface (>600m^2/g)
- ✓ Presence of sp^3 carbon - disorder

TEGO Functionalization

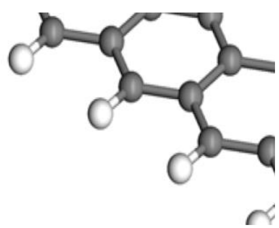
H_2 generator



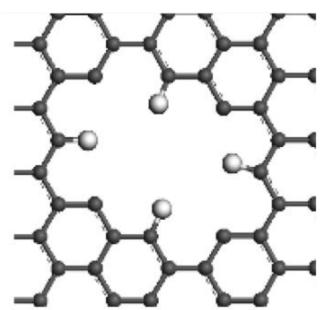
Heat treatment at 800°C



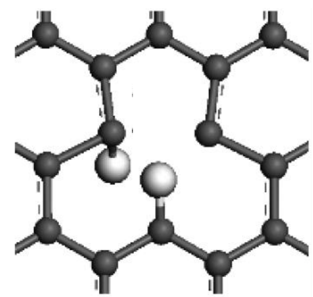
Neutron spectroscopy investigation



Edges



Inner voids



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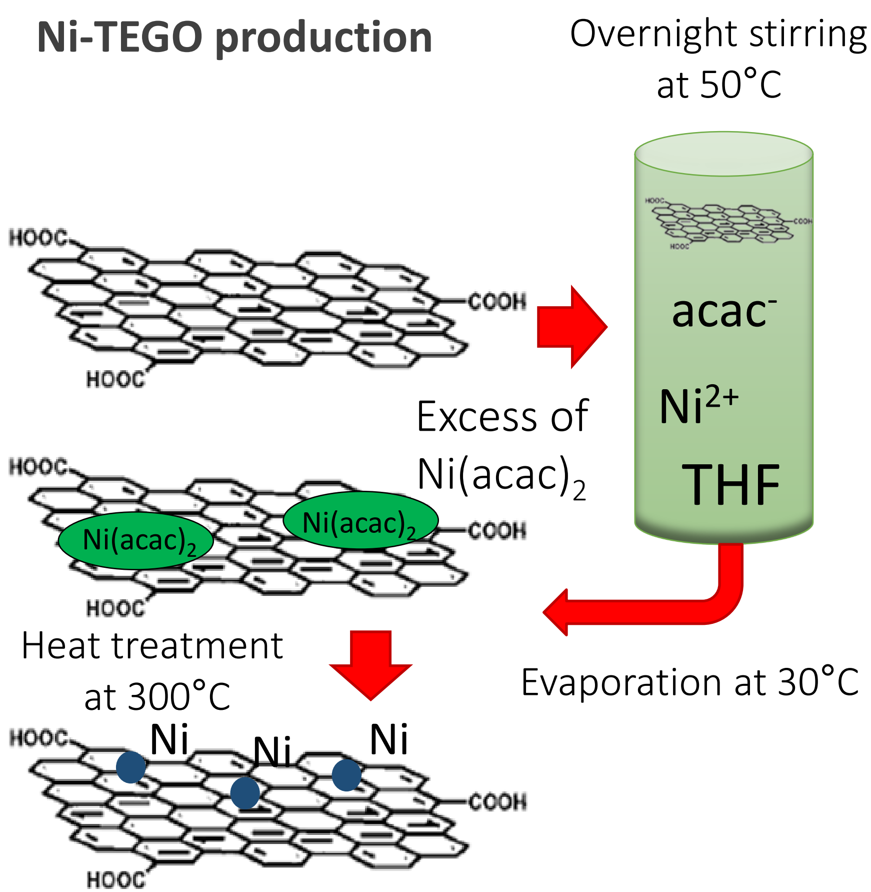
NEUTRONS FOR SCIENCE

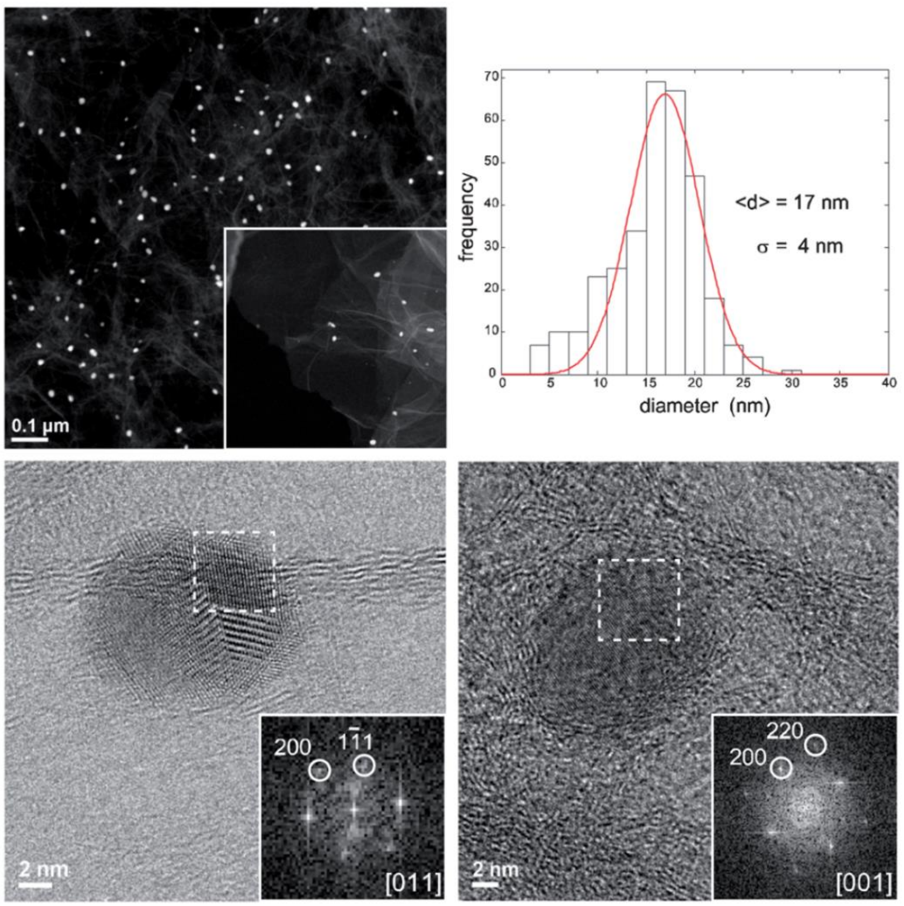
C. Cavallari, D. Pontiroli et al, Phys. Chem. Chem. Phys. 18, 24820 (2016)

D. Pontiroli , M. Riccò et al., J. Phys. Chem. C 118, 7110 (2014)

TEGO Functionalization

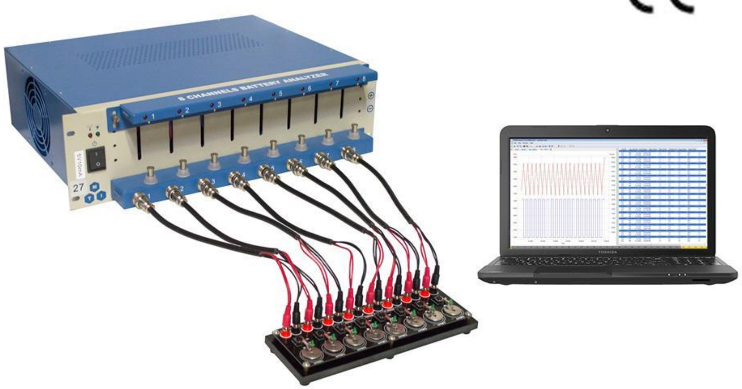
Ni-TEGO production



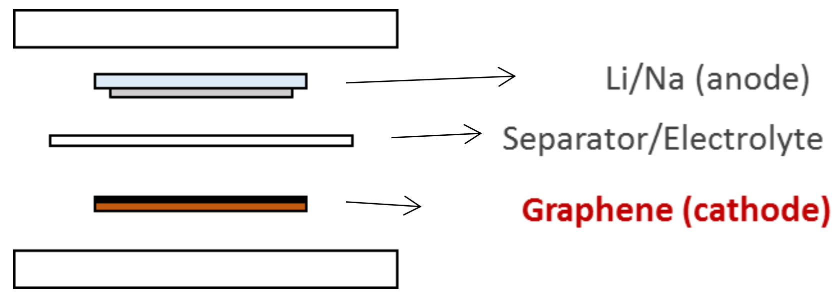


M. Gaboardi, D. Pontiroli et al, J. Mater. Chem. A 2, 1039 (2014)

TEGO derivatives as electrode materials

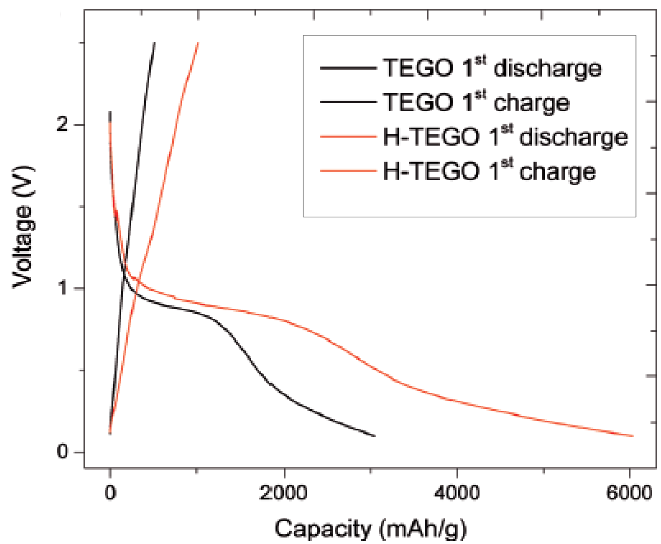


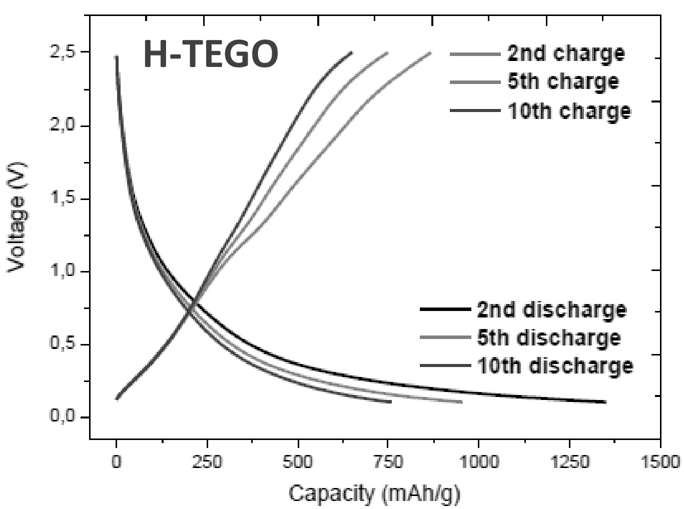
Half cell



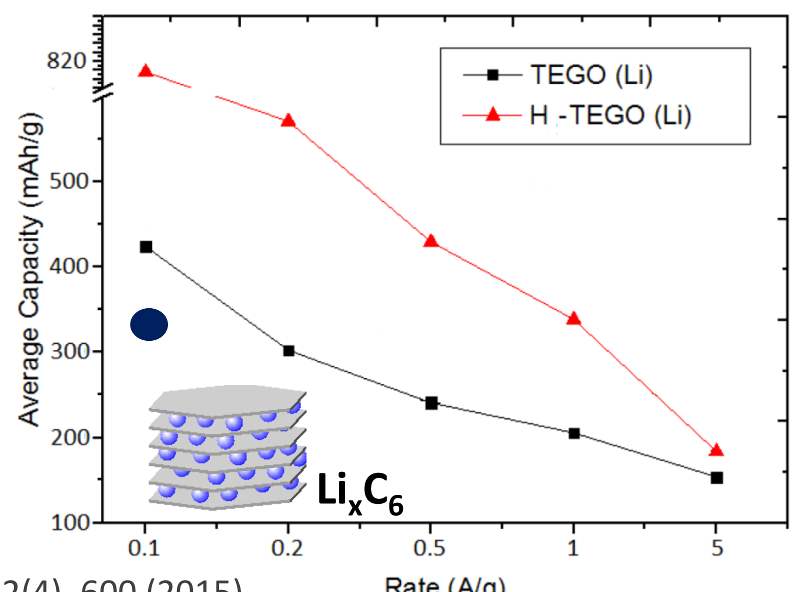
- ✓ Standard CR-2032 coin cells
- ✓ Li-ion half cells: use of 1M $LiPF_6$ in DMC/EC (1:1 wt%)
- ✓ Na-ion half cells: use of 1M $NaPF_6$ in DMC/EC (1:1 wt%)

TEGO Derivatives in Li-ion batteries



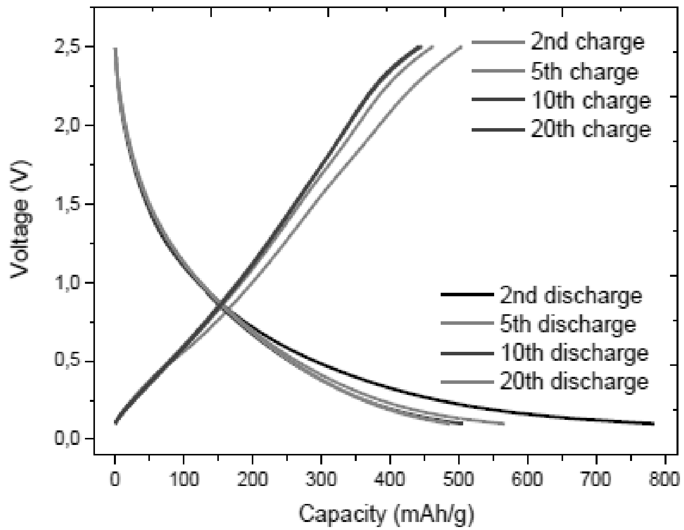


- ✓ High irreversible capacity loss at the 1st cicle
- ✓ Slope suggests presence of capacitive storage effect
- ✓ High rate capability and reliability (as compared with graphite)

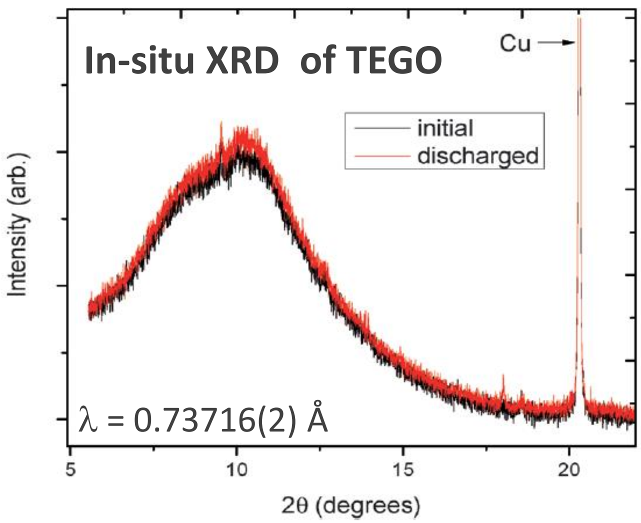


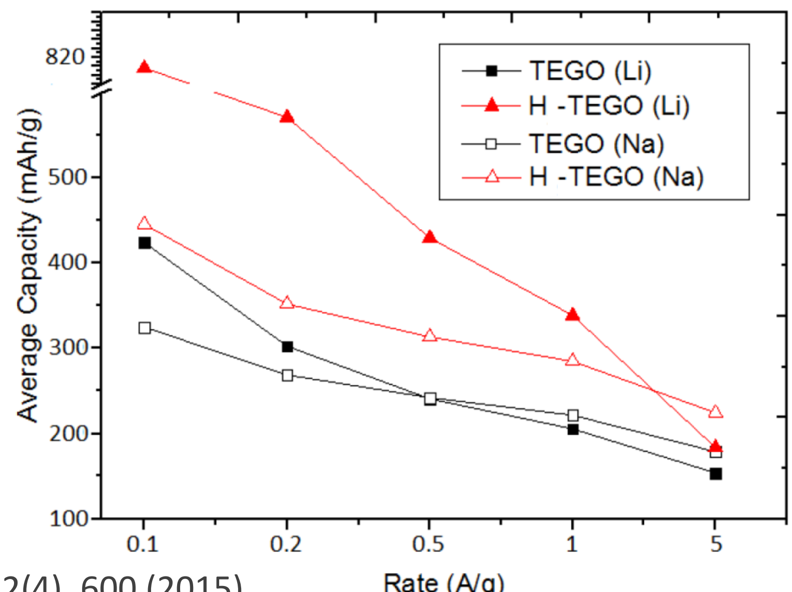
J. A. Pramudita, D. Pontiroli, N. Sharma et al, ChemElectroChem 2(4), 600 (2015)

TEGO Derivatives in Na-ion batteries



- ✓ Graphene allows Na intercalation and works also in Na-ion half-cells (NB: graphite DOES NOT intercalate Na!)
- ✓ Performances are similar to graphene LiBs
- ✓ No formation of crystalline region upon discharge/charge

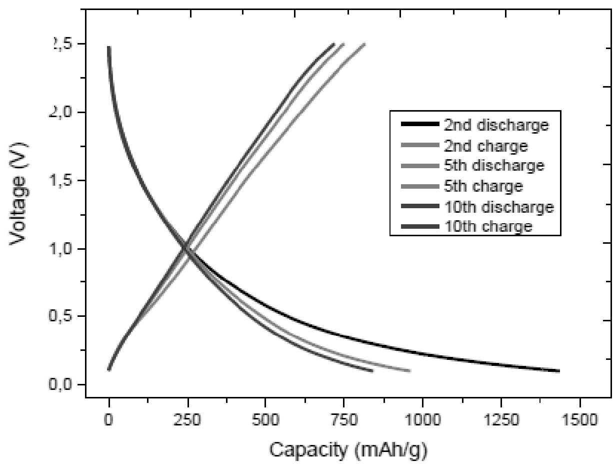




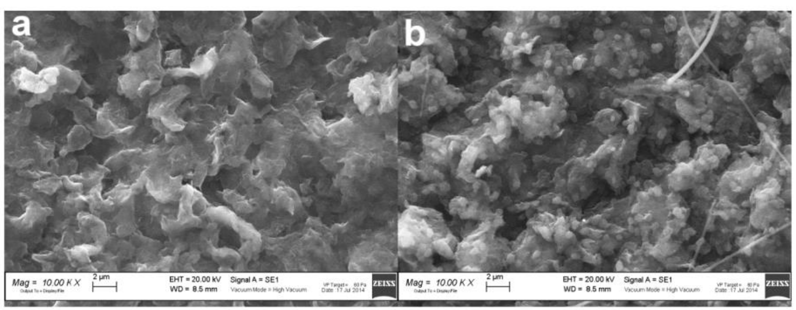
J. A. Pramudita, D. Pontiroli, N. Sharma et al, ChemElectroChem 2(4), 600 (2015)

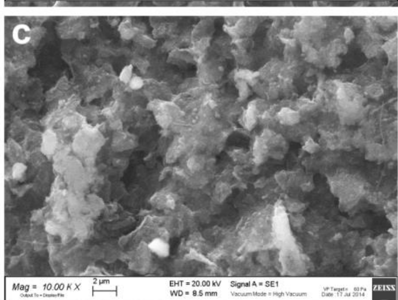
Ni-TEGO in LIBs and SIBs

Ni-TEGO (NiC80) in SIBs

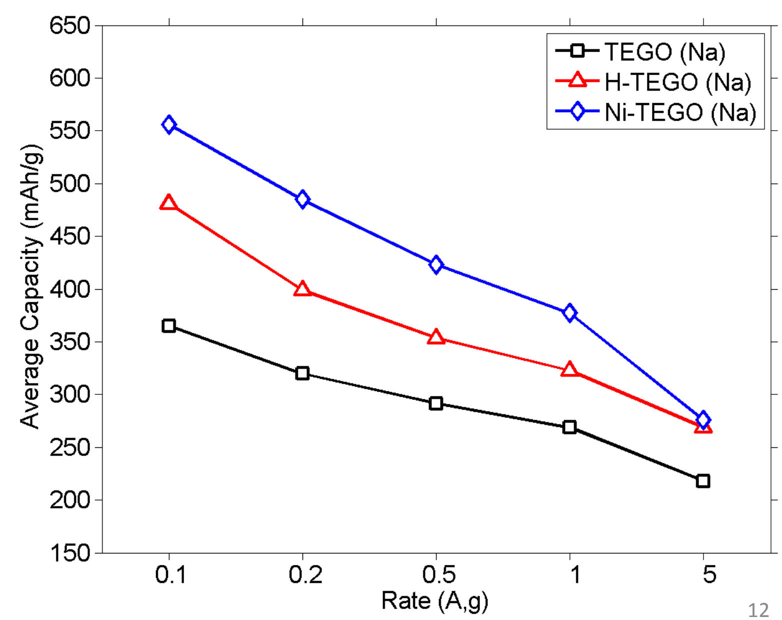


- ✓ Better performances of Ni-TEGO as negative electrode in Na-ion half-cells
- ✓ Capacity of 520 mAh/g after 20 cycles (at 100 mA/g) with ~97% coulombic efficiency
- ✓ SEM shows presence of small Na-rich aggregates (0.2-2 µm)





a) 1st discharge
b) 1st charge
c) after 20 cycles, charged

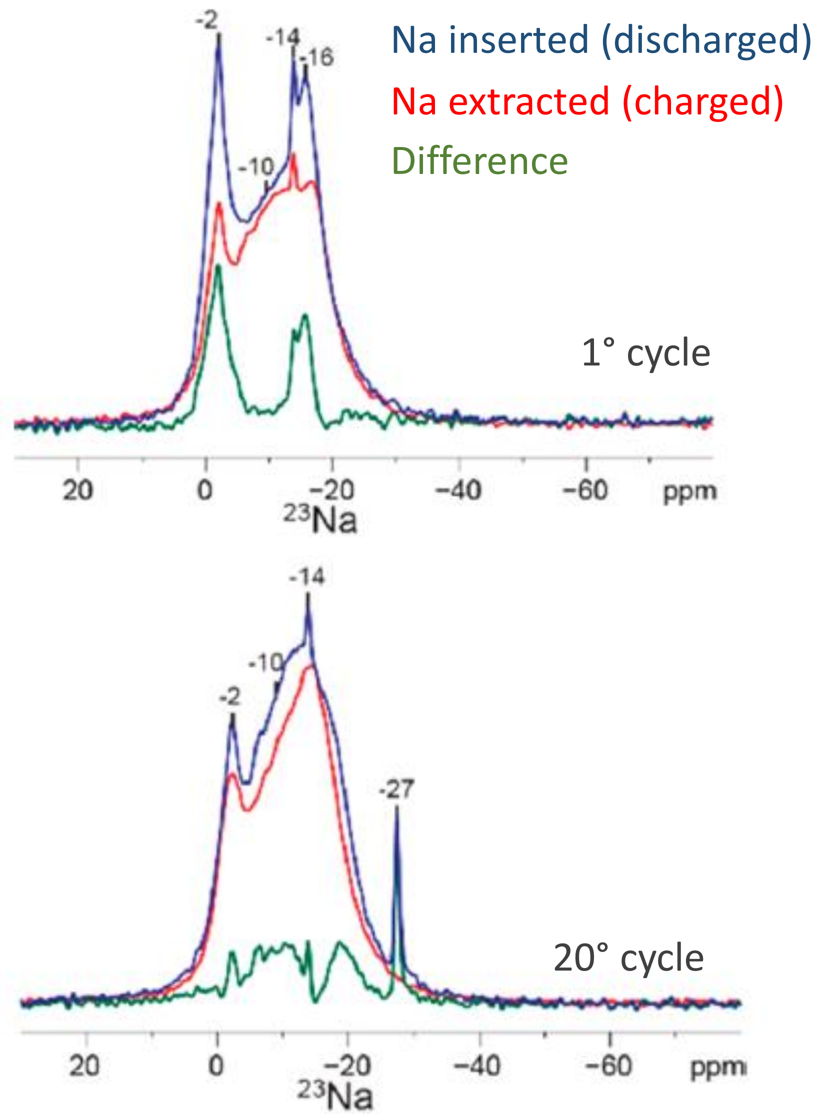


J. A. Pramudita, D. Pontiroli, N. Sharma et al, ChemElectroChem 2(4), 600 (2015)

Mechanism of Na insertion/extraction

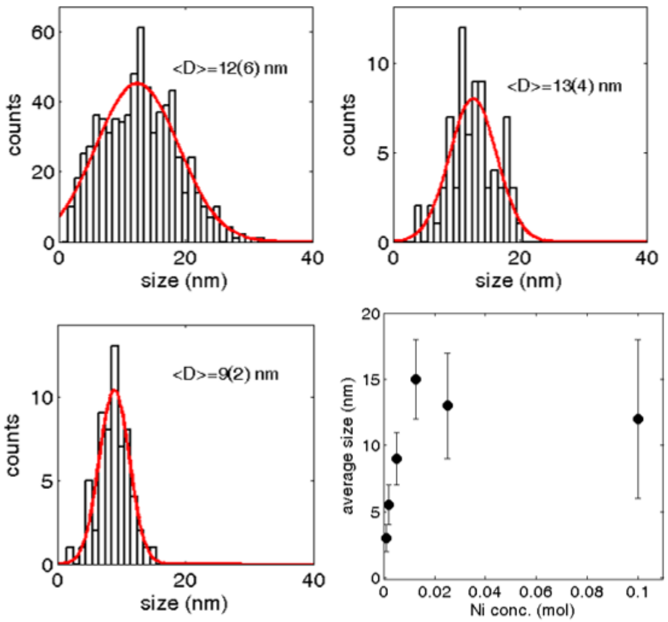
UNSW AUSTRALIA

- ✓ Na environment on and between the TEGO surface after charge/discharge cycles was investigated by means of ^{23}Na NMR MAS
- ✓ During 1st cycle, three mobile sites at -2, -14 and -16 ppm and one immobile site at -10 ppm are present
- ✓ During 20th cycle, three mobile sites at -2, -14 and -27 ppm and one immobile site at -10 ppm are present
- ✓ The immobile site correlates with the large irreversible loss after the 1st cycle
- ✓ The decrease of mobile sites correlates with the fade of the performances during cycling

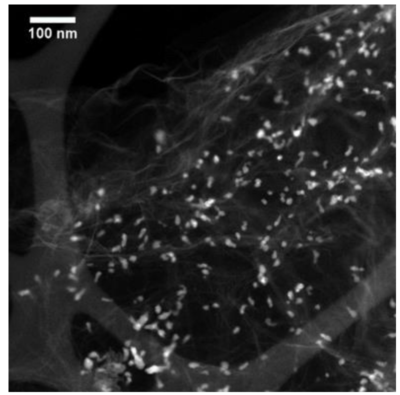


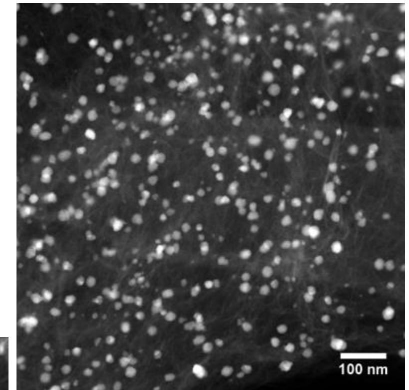
J. A. Pramudita, D. Pontiroli, N. Sharma et al, ACS Appl. Mater. Interfaces 9 (1) , 431 (2017)

The role of Ni Nanoparticles



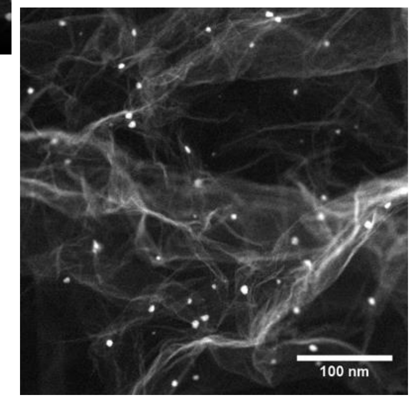
NiC$_{10}$



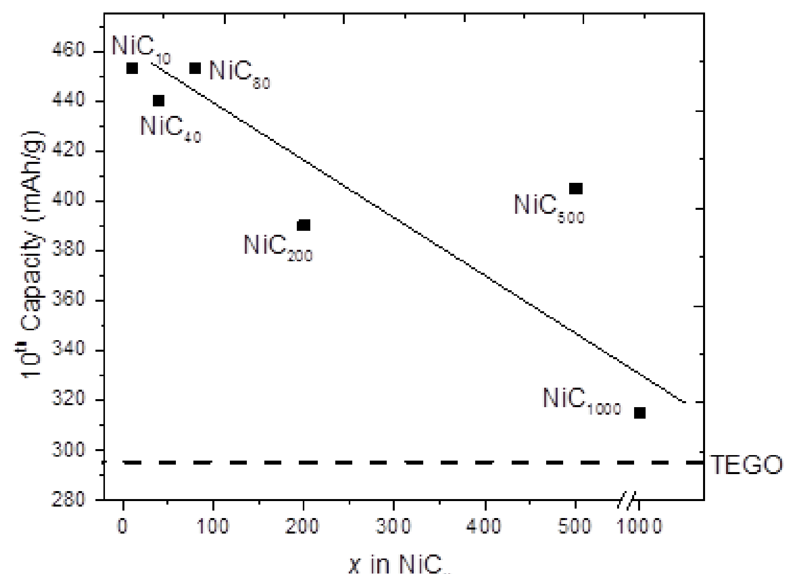


NiC$_{40}$

NiC$_{200}$



- ✓ Ni-NPs dimensions depends on the Ni concentration as well as on the annealing time
- ✓ Ni-NPs size ranges from 4(2) to 15(4) nm and shows saturation behaviour
- ✓ Ni-NPs play a role in the Ni-TEGO electrode capacity and in the rate capability



J. A. Pramudita, D. Pontiroli, N. Sharma et al, manuscript in preparation

Conclusions

- ✓ Graphene based materials enable **alternatives to Li-ion batteries**
- ✓ Chemical graphene (TEGO) and its derivatives (H-TEGO and Ni-TEGO) behave as **good negative electrodes for both Li- and Na-ion batteries**.
- ✓ Decoration of TEGO with Ni NPs clearly improves the performances in **Na-ion batteries**
- ✓ The mechanism of Na insertion/extraction in TEGO **comprises the population of both mobile and immobile sites**, the latter probably involved in **SEI formation**

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Thank you for your attention!