

Study of Ni decorated Graphene based Electrodes for Asymmetric Supercapacitors

¹A. Morengi, ¹G. Magnani, ¹S. Scaravonati, ¹M. Sidoli, ²G. Berton, ¹M. Riccò, ¹D. Pontiroli.

¹ Nanocarbon Laboratory, Department of Mathematical, Physical and Computer Sciences, University of Parma, Via Parco Area delle Scienze 7/A, Parma, Italy

² IMEM-CNR, Parco Area delle Scienze, 37/A, Parma, Italy

Abstract

Carbon based supercapacitors are electrical energy storage systems. With respect to batteries, these can achieve higher specific power, greater efficiency, longer average life but a smaller specific energy [1]. In order to increase the stored energy, pseudocapacitive effects and asymmetric configurations can be exploited. The former increase the capacitance of the device [2], the latter allows to extend the working voltage window over the electrolyte limits [3], therefore enhancing the specific energy. In the current work, our aim is to improve the energy stored in a porous defective graphene-based asymmetric supercapacitor, by introducing a faradic contribution in the positive electrode and coupling it with a purely capacitive negative electrode. Both electrodes are manufactured with graphene obtained by thermal exfoliation of graphite oxide (TEGO) [4]. A remarkable increase of specific capacitance of the positive electrode up to 1350(30) F/g, arising from battery-like redox contributions, has been obtained by anchoring nickel nanoparticles (Ni-NPs) to TEGO defects [5], which convert to Ni(OH)₂ sheets once exposed to aqueous electrolyte (KOH 3.5 M). The asymmetric device proved to be stable in an extended potential window of 1.7 V.

Synthesis

TEGO

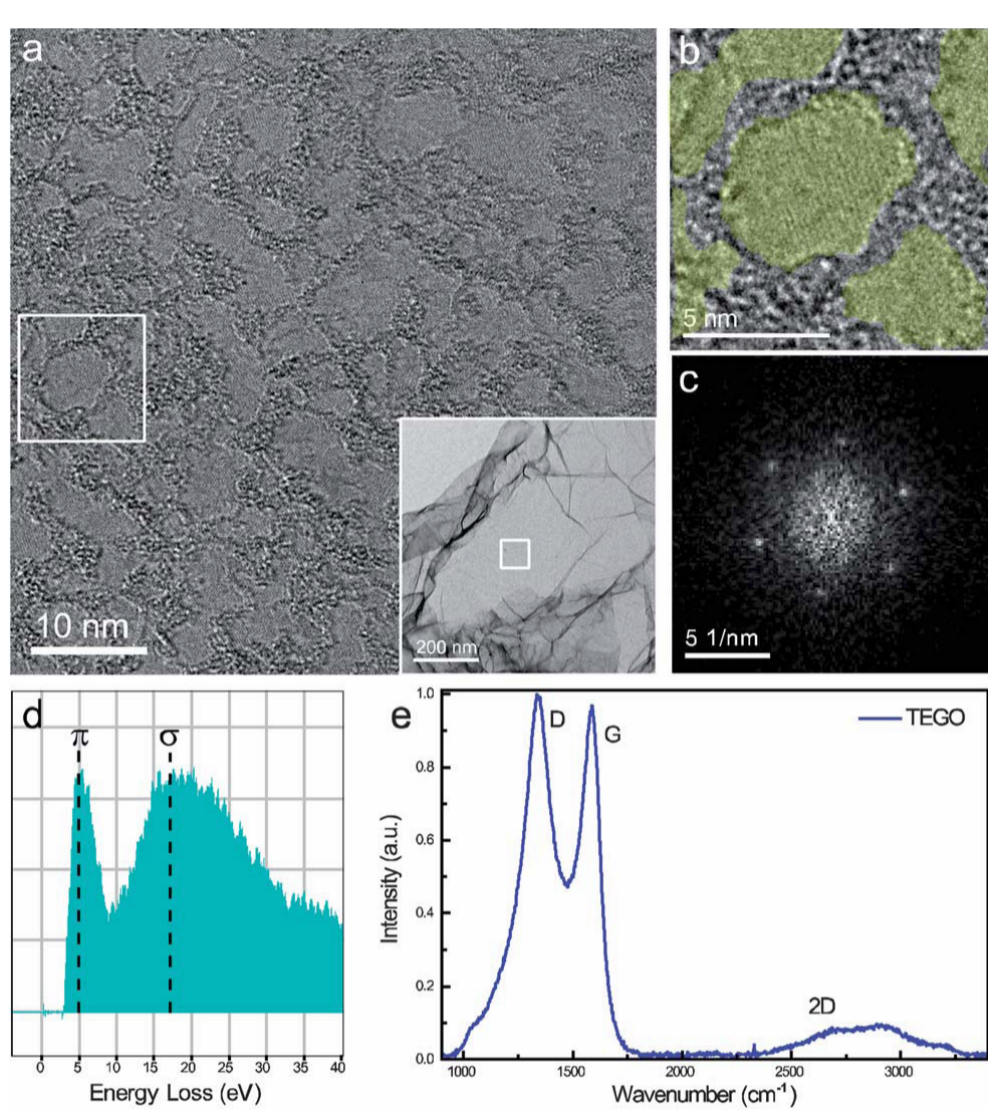
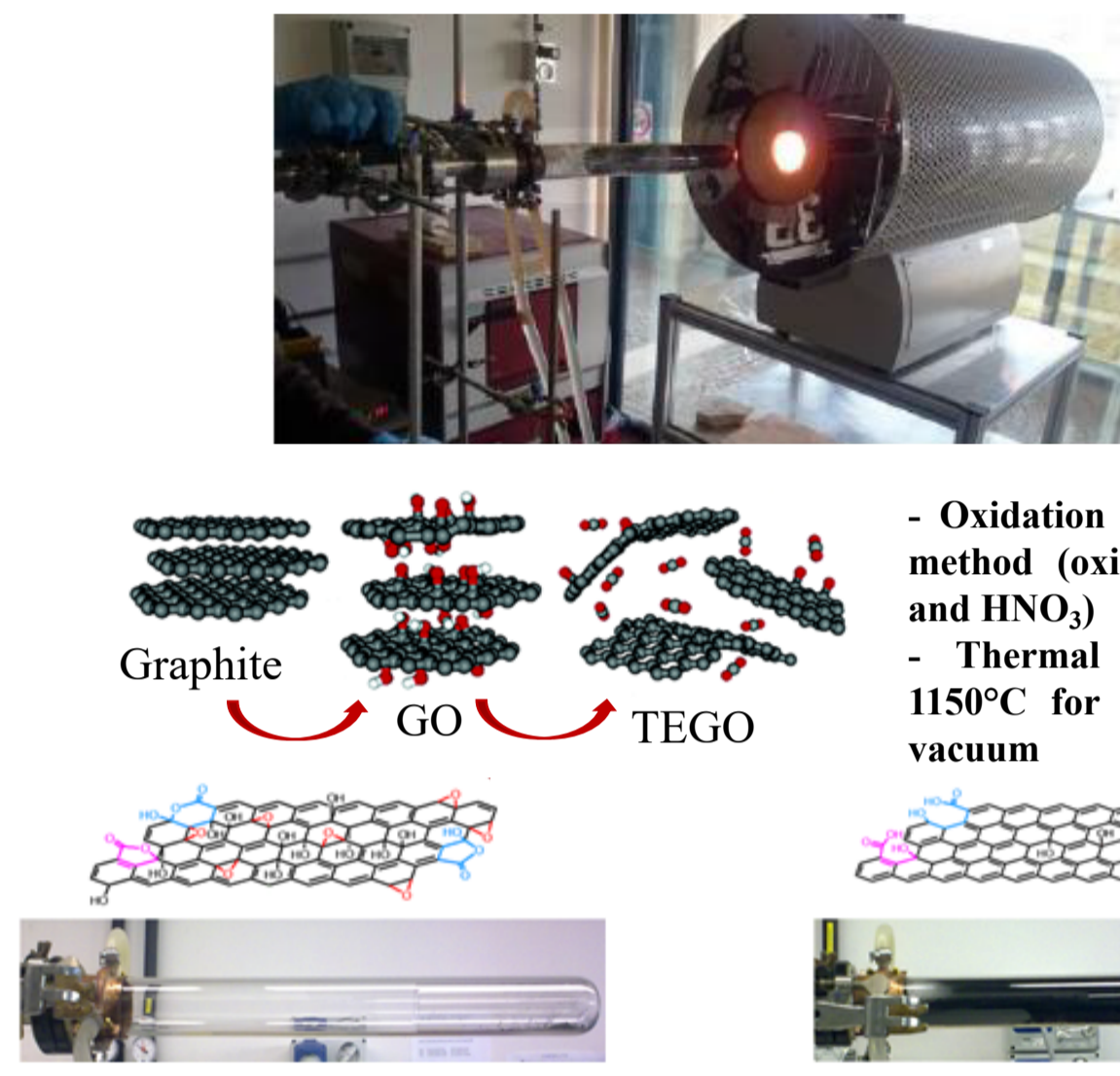


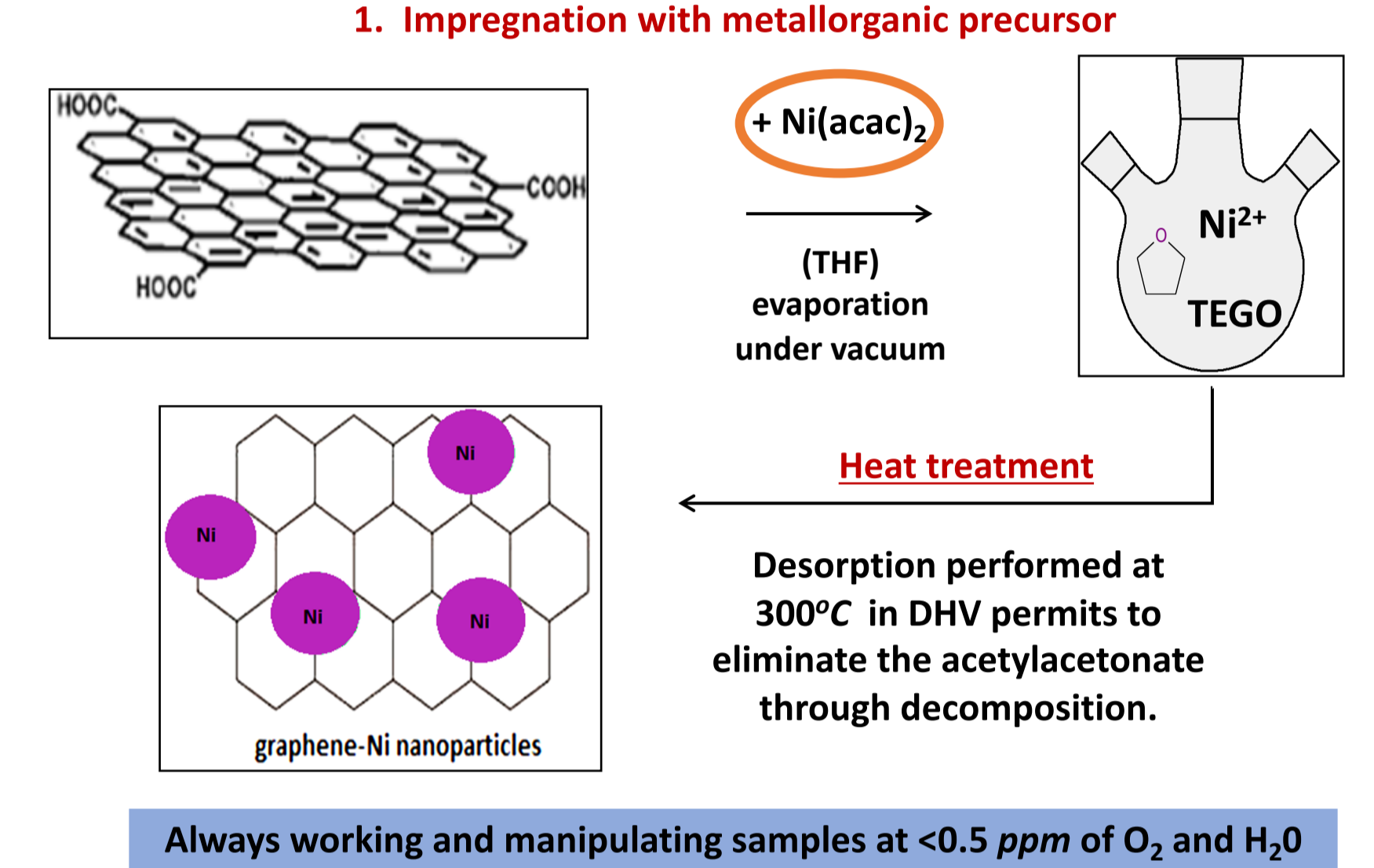
Fig. 1: (a) 80 kV HRTEM image from a flat TEGO region. Small very thin domains are visible, which are surrounded by a thicker network due to residual GO after exfoliation. (b) Zoom of a portion of the film, single layers highlighted in yellow. (c) FFT with sharp {1100} spots. (d) Average EEL spectrum from the whole region in. The position of the π plasmon is in agreement with 1-5 layers (superposition of the thin TEGO domains and the thicker GO residual). (e) Raman spectrum of as-synthesised TEGO. $I_D/I_G=1.56$ which gives an average sp^2 domain of 12.3 nm.[5]

Synthesis of TEGO



- Oxidation of graphite with Brodie method (oxidizing reagents NaClO₃ and HNO₃)
- Thermal exfoliation of GO at 1150°C for 30 min under dynamic vacuum

Nickel decoration of TEGO



Always working and manipulating samples at <0.5 ppm of O₂ and H₂O

TEM Analysis

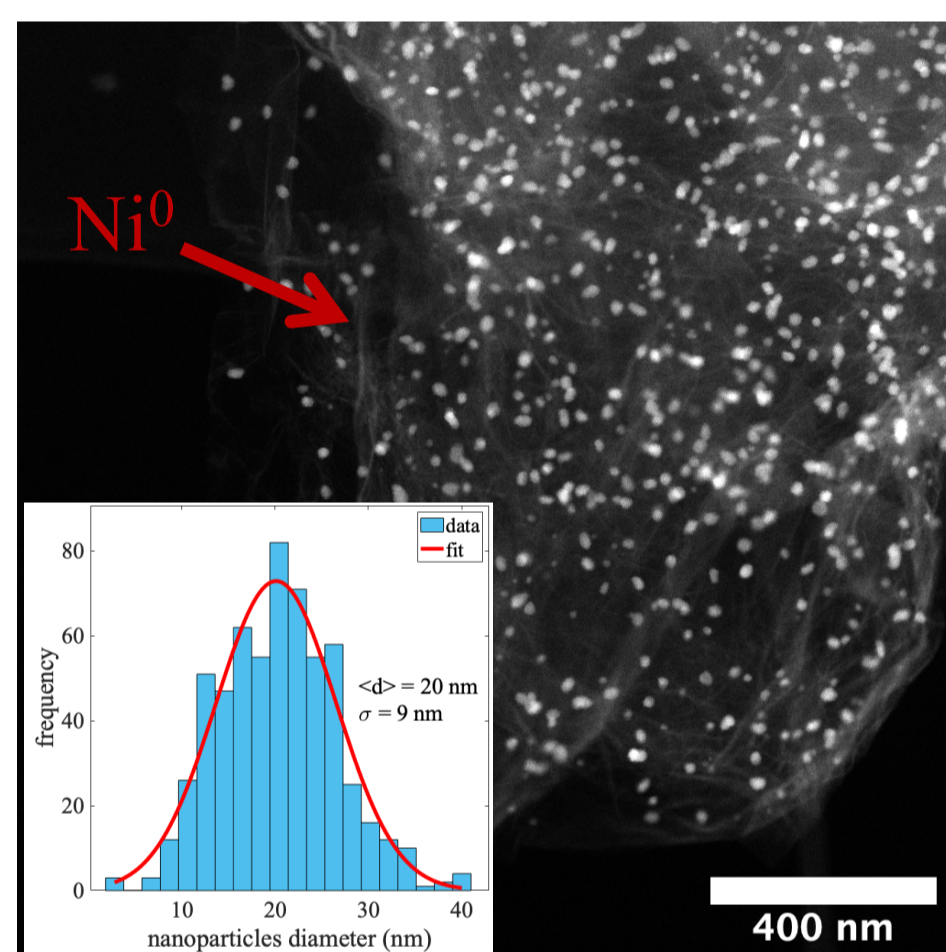


Fig. 2: STEM image of Ni-TEGO material before its electrochemical oxidation and characterization. The sample prepared have a Ni:C ratio of 1:10 and metallic Ni-NPs, which are anchored in graphene defects, have a diameter of 20 nm.

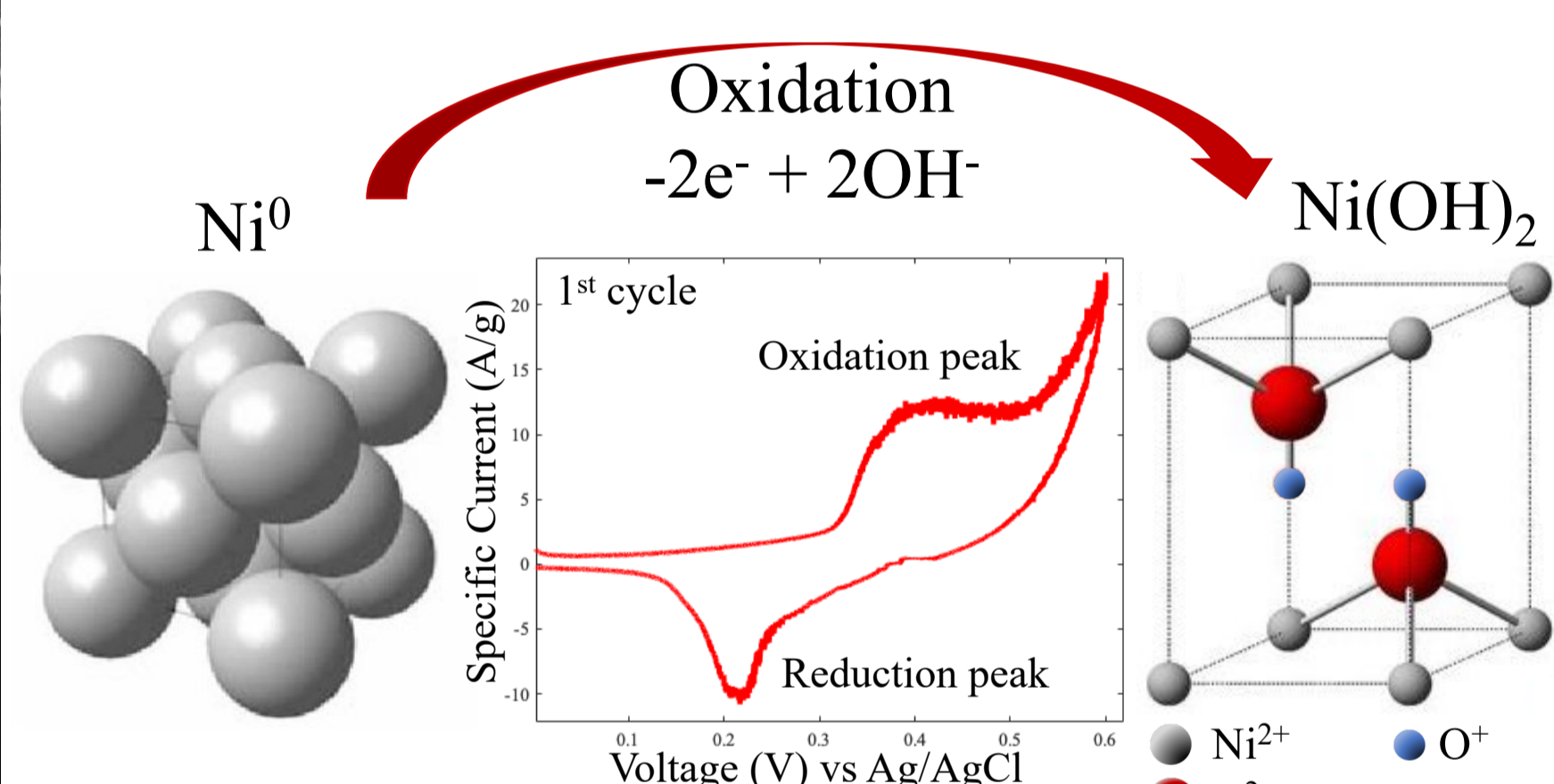


Fig. 3: During the first cycle of cyclic voltammetry, an irreversible oxidation occurs, oxidising metallic Ni-NPs into nickel hydroxide. In fact, the area of the first-cycle oxidation process is greater than twice the area of the reduction step. Since that, the electrochemical behaviour becomes completely reversible as we can see from Fig. 7.

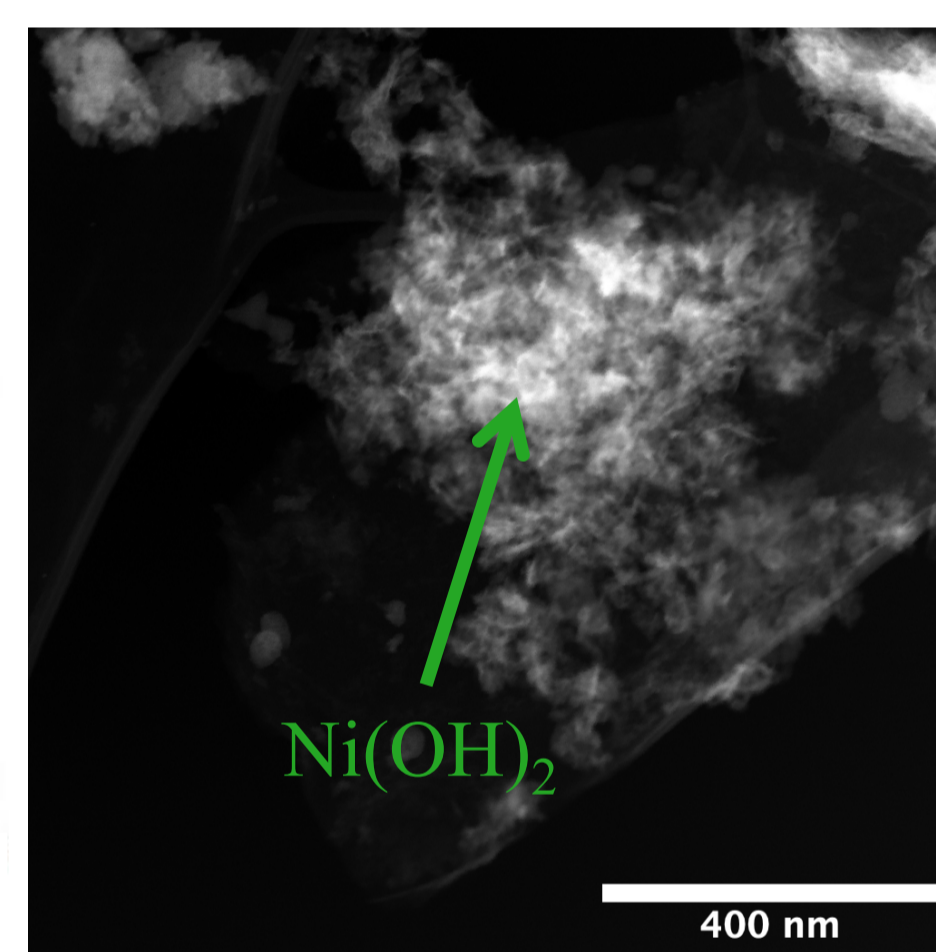


Fig. 4: STEM image of the Ni-TEGO electrode after few voltammetric cycles in the three-electrode cell. Ni-NPs, getting oxidised into nickel hydroxide, appear as thin sheets adhering to graphene and covering it totally.

XRD Analysis

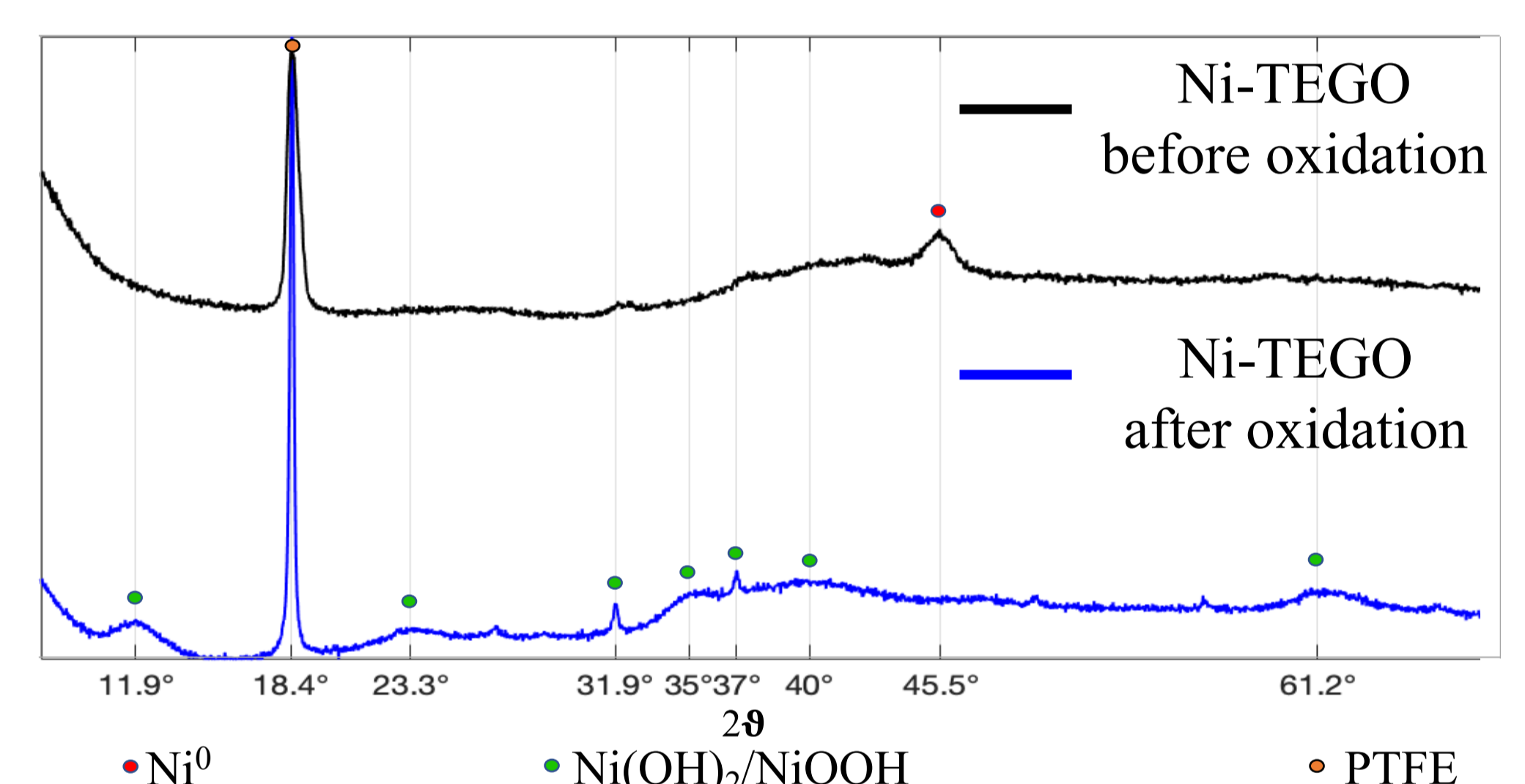


Fig. 5: The collected diffractograms, before and after voltammetric cycles, confirm the formation of nickel oxidized species and the disappearance of the metallic one. The more intense peak at 2θ=18° belongs to the binder (PTFE) used for producing the electrodes.

Three-electrode Cyclic Voltammetry Analysis

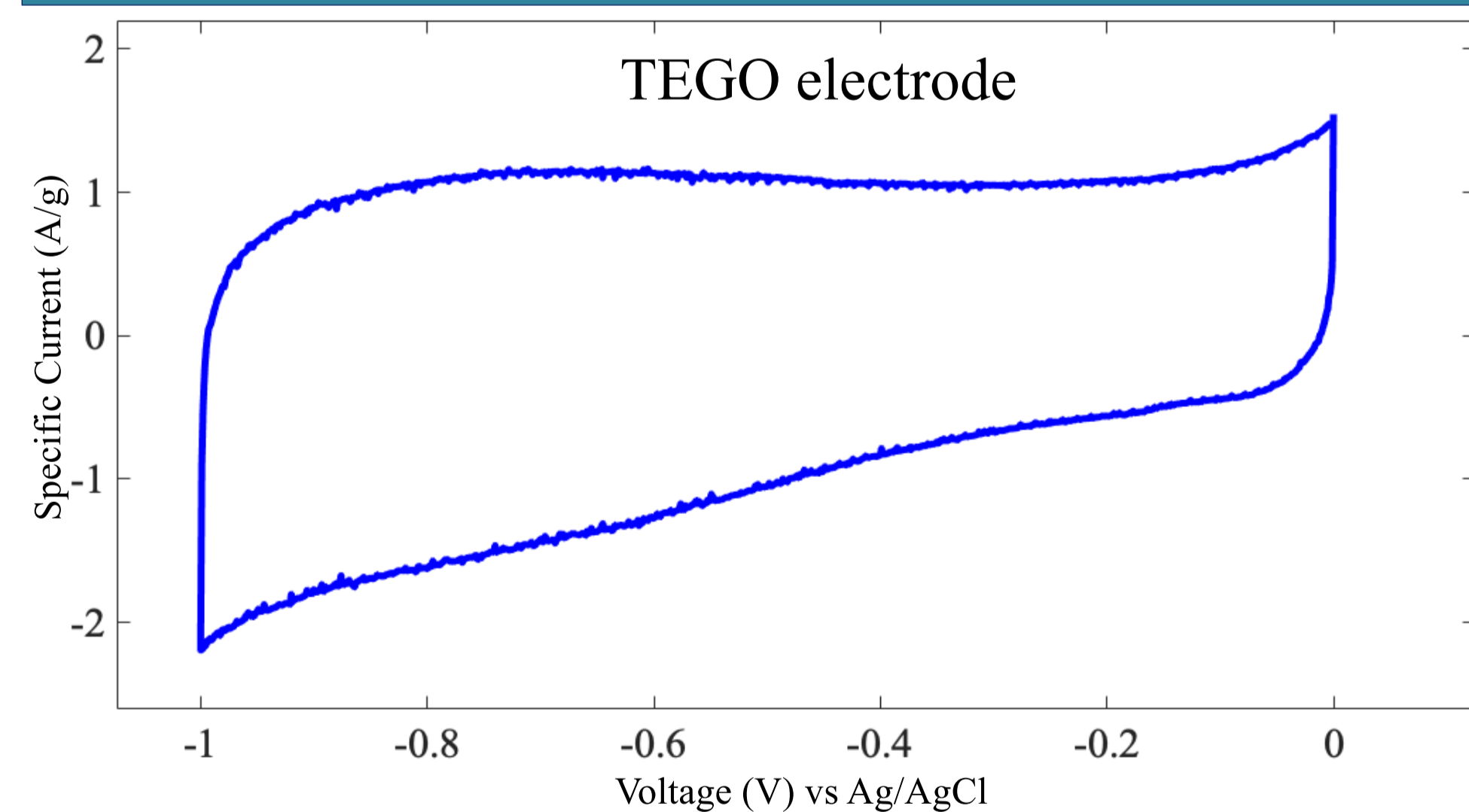


Fig. 6: Three-electrode cyclic voltammetry curve of TEGO electrode at 10 mV/s rate. It exhibits a specific capacitance of (103 ± 5) F/g. The quasi-rectangular shape confirms the mainly capacitive behaviour of the TEGO electrode. In the asymmetric supercapacitor configuration, graphene electrode plays the role of negative electrode.

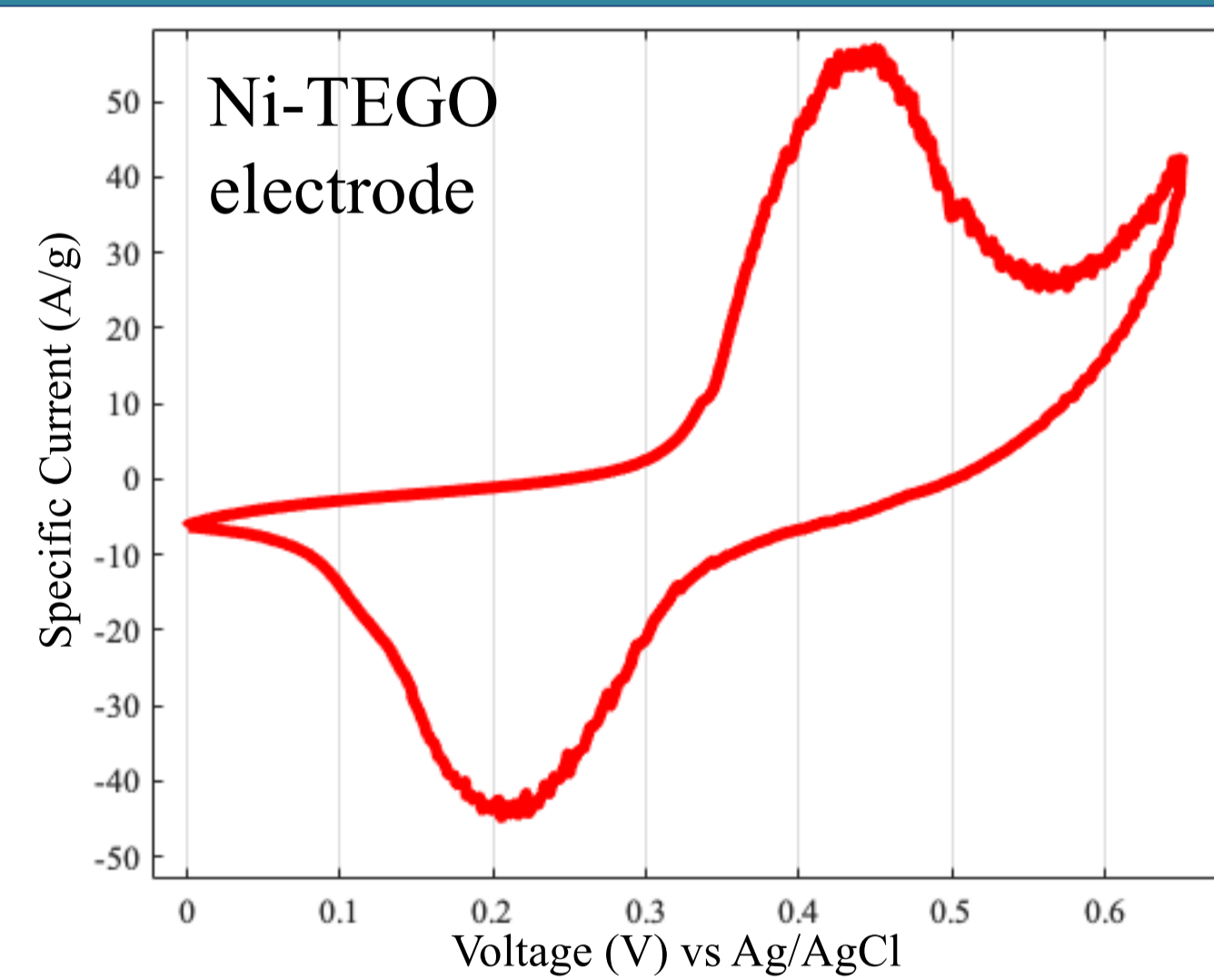


Fig. 7: Three-electrode cyclic voltammetry curve of Ni-TEGO electrode at 10 mV/s rate. It exhibits a specific capacitance of (1350 ± 30) F/g. During the oxidation process the Ni(OH)₂ oxidise into NiOOH and otherwise in the reduction step. The quasi-symmetrical area below the peak lines testifies the good reversibility of the system. In the asymmetric supercapacitor configuration, this electrode plays the role of positive electrode.

Asymmetric Supercapacitor

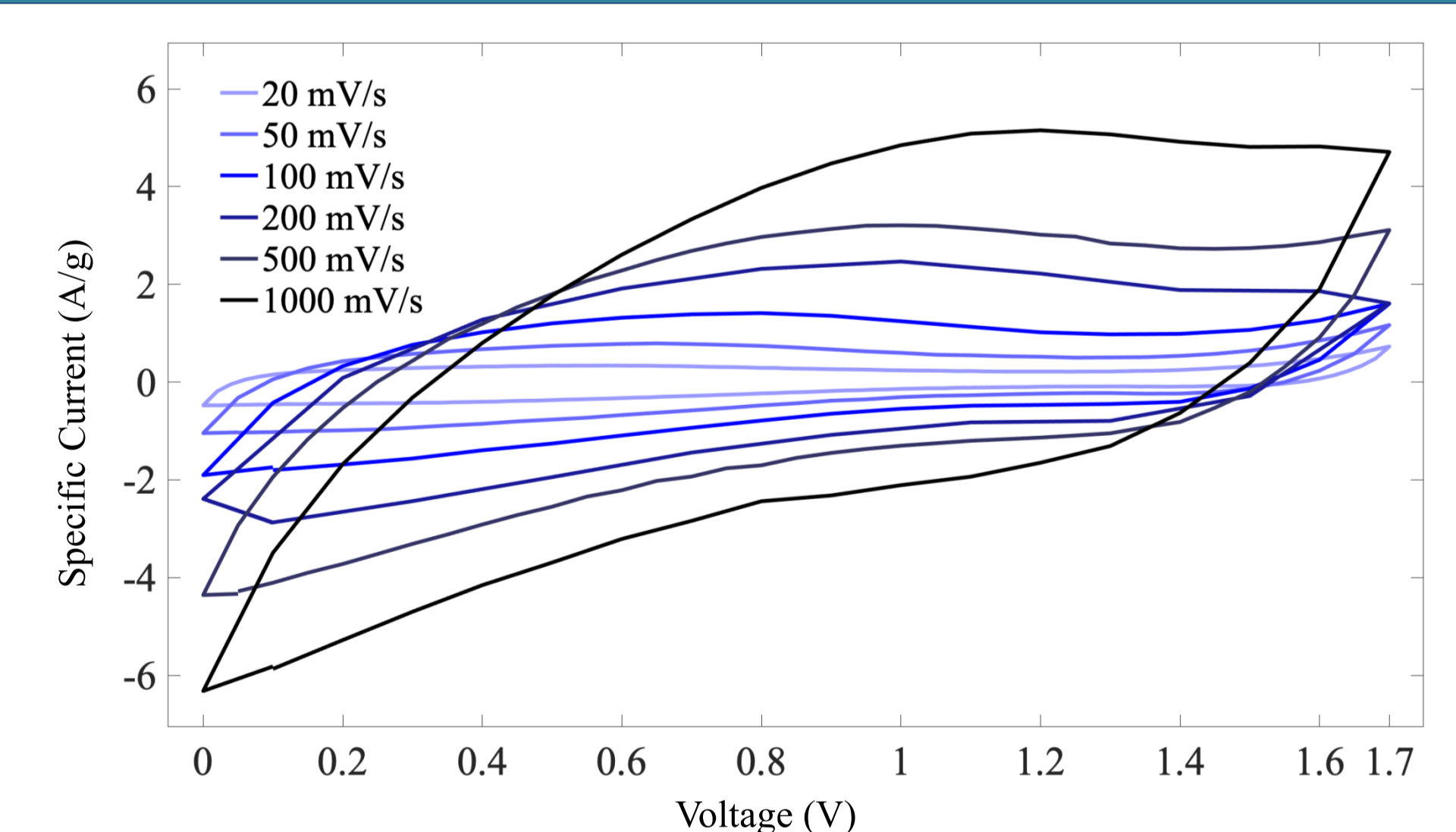


Fig. 8: The asymmetric supercapacitor exhibits an enhanced stability on a 1.7 V window, overcoming the limit due to the water electrolyte (KOH 3.5 M) we used, that is around 1.2V. The device is built balancing the capacitance of the two electrodes in order to use the maximum capacitance of Ni-TEGO electrode.

Conclusions

In this work we presented a method for building a graphene-based asymmetric supercapacitor, which can overcome the water electrolysis voltage limit, therefore, enhancing its specific energy. Moreover, the battery-like electrode is synthesized through the 1st cycle oxidation of metallic Ni-NPs well dispersed and anchored to the graphene sheets, result of a controlled thermal decomposition of a nickel precursor. This method allowed us to maximize the specific surface of the Ni(OH)₂ redox active species, consequently enabling the exhibition of an excellent specific capacitance of almost 1350 F/g at 10 mV/s, which decreases to 420 F/g at a rate of 200 mV/s. The performance investigation of the asymmetric supercapacitor is currently in progress.

REFERENCES

- Béguin F., et al., "Carbons and electrolytes for advanced supercapacitors." *Advanced materials*, (2014), 26(14), 2219-2251.
- Conway B. E., et al., "Transition from "supercapacitor" to "battery" behavior in electrochemical energy storage." *Journal of the Electrochemical Society*, (1991), 138(6), 1539-1548.
- Dai Z., et al., Cell voltage versus electrode potential range in aqueous supercapacitors. *Scientific reports*, (2015), 5, 9854.
- Riccò M., Pontiroli D., Mazzani M., Chouair M., Stride J. A., & Yazayev, O. V., Muons probe strong hydrogen interactions with defective graphene. *Nano letters*, (2011), 11(11), 4919-4922.
- Gaboardi M., et al., Decoration of graphene with nickel nanoparticles: study of the interaction with hydrogen. *J. Mater. Chem. A*, (2014), 2, 1039.
- Morengi A., et al., Study of Ni decorated Graphene based electrodes for Asymmetric Supercapacitors. *In preparation*.

CONTACT PERSON

Alberto Morengi
alberto.morengi@unipr.it

Daniele Pontiroli
daniele.pontiroli@unipr.it