

# Atom-by-atom structural characterization of nano-materials using aberration-corrected electron microscopy

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## Abstract

A comprehensive nanoscale understanding of new materials is critical for their current and future applications in energy storage devices. In this project, electron microscopy and other techniques were employed to extensively characterise the thermal progressions of nickel-iron containing (Ni-Fe) LDH nanomaterials. Amorphisations were examined by HR-TEM and STEM. The versatility of this characterisation approach, and its versatility, are evident from the depth of characterisation. Findings and experience were applied to the electrochemical characterisation of graphene electrodes and the pseudocapacitor behaviour of printed MnO<sub>2</sub>-graphene devices. Both cyclability and capacitance were examined for a variety of configurations, with chloride salt PVA-based gel electrolytes producing the most favourable results.

## Introduction

As society becomes more conscious of the negative environmental consequences associated with the everyday consumption of energy, produced in the main by the unsustainable combustion of fossil-fuels, there is an increased demand for “clean” energy generated from renewable sources. Many such sources are inconstant and unreliable, leading to difficulties in meeting consumer demand. Chief among the identified feasibility challenges is our relative inability to store energy efficiently, meaning that energy supply is dependant on unreliable external factors. New material families with novel properties may be exploited to produce new and exciting energy-storage devices. However, our ability to employ nano-materials in new devices is limited by our understanding of their structure. Advances in electron microscopy, allowing for atomic resolution and identification, are herein used to structurally characterise transition metal carbides (MXenes) and layered double hydroxides (LDH) composites. Findings are subsequently employed in the “proof-of-concept” trails of MnO<sub>2</sub>-graphene electrochemical super-capacitors, a new breed of energy storage device.

## Main Objectives

### 0.1 Atom-by-atom structural characterisation of MXene and LDH structures

1. To examine the topographical features of various MXene crystals by means of scanning electron microscopy (SEM)
2. To perform crystallographic and structural analysis on such structure by aberration-corrected Transmission Electron Microscopy
3. To employ Electron Energy-Loss Spectrometry (EELS) and Energy-dispersive X-ray spectroscopy (EDX) to determine the chemical identity of these structures
4. To use the above techniques to qualitatively analyse the effect of annealing on the MXene-LDH hybrids

### 0.2 Fabrication of MnO<sub>2</sub>-graphene double-layer capacitors

1. To print, onto a photographic substrate and from suspension, graphene and MnO<sub>2</sub> devices
2. To examine the electrical performance of these devices by means of Cyclic Voltammetry (CV) and Charge-Discharge Cycles.
3. To synthesise various salt and acid based gel-electrolytes
4. To apply these to MnO<sub>2</sub>-graphene double-layer capacitors and before being subject to CV analysis.

## Experimental Method

### 0.3 Microscopy and structural characterisation

Samples of Mg-Al LDH were synthesised according to recipes found in the literature. The formation of large platelets was achieved by precipitation following reflux, and separation by centrifugation (3,000 rpm/10 min). Samples were drop-cast onto copper TEM-grids and imaged in a FEI Titan300 (FEI, Oregon, USA), operated at 300 kV. In-situ heating TEM experiments were conducted using a DENS Solutions Wildfire TEM holder. Samples were subjected to the following heating procedure, 30 °C (10 min), 250 °C (120 min), 450 °C (120 min), and 850 °C (120 min). All temperature ramps were at 10 °C/min.

### 0.4 Analysis of supercapacitors

Capacitors were fabricated by ink-jet printing onto various substrates, substituting MnO<sub>2</sub>/graphene suspensions for the standard ink. Symmetric supercapacitors were assembled. Cyclic voltammetry experiments were performed in a potential range of 0 to 1 V versus Ag/AgCl. Galvanostatic charge-discharge experiments were performed in a potential range 0 to 1 V vs Ag/AgCl. Experiments were repeated with PVA gel-electrolytes (KCl, LiCl, phosphoric acid) manufactured from various recipes available in the literature. Further analysis was conducted on depositions of MnO<sub>2</sub> on conductive glass.

## Results

### 0.5 In-situ analysis of LDH platlets and temperature response

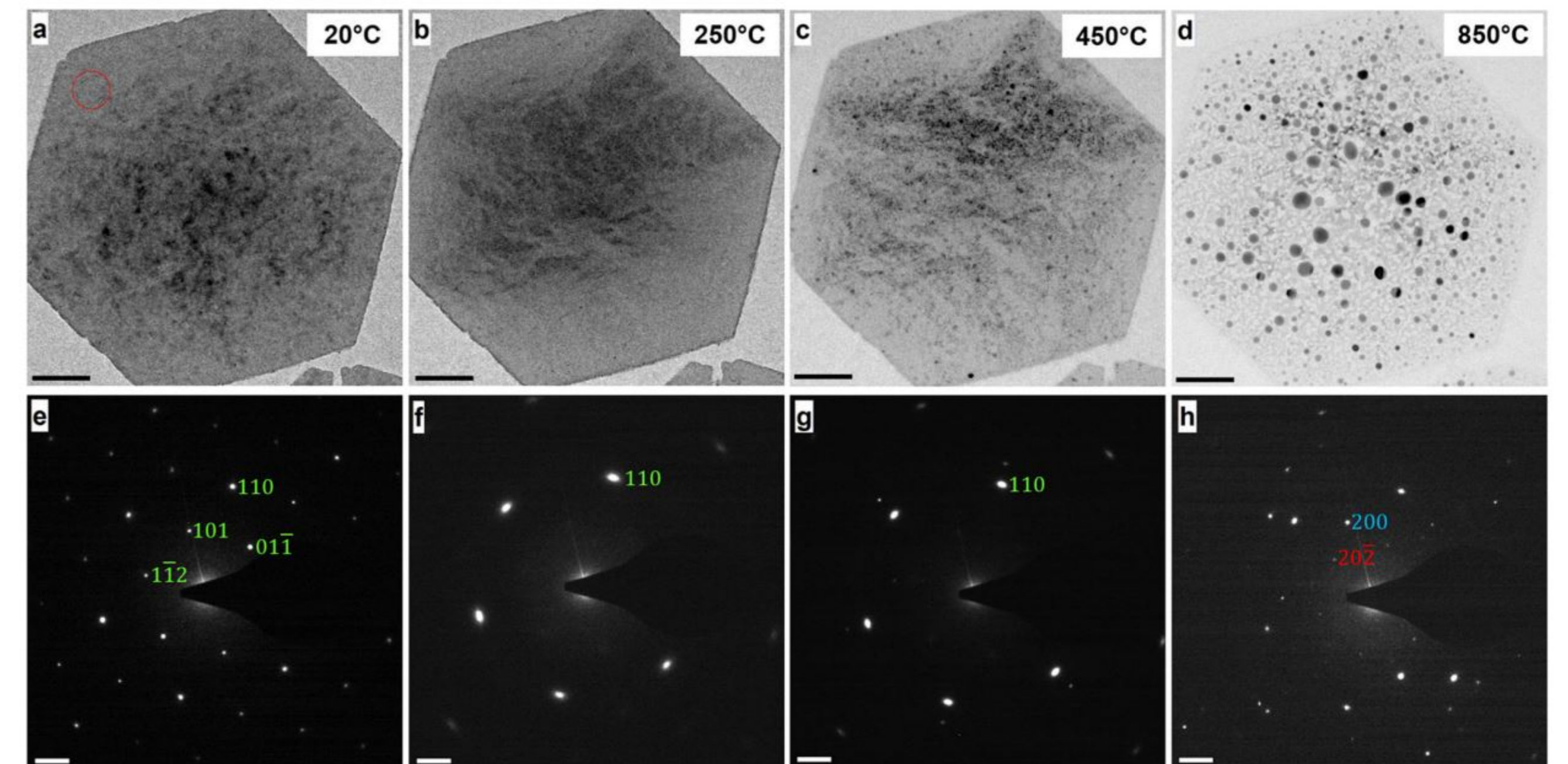
Temp (°C)	Observation
20	—
250	Collapse of (101), (011̄), and (112̄)
450	Evolution of spherical particles, dist. random
850	Emergence of the {200} and {220}

**Table 1:** Observations on the change of the platelet crystallographic structure as a result of increasing temperature. Note rearrangement of LDH structure into a new crystallographic arrangement at 250 °C and again at 850 °C

formed between 250 and 450 °C. It is posited that these morphological changes are a result of the loss of moisture from the structure— this may be expedited by the intensity of the electron beam on

Aberration corrected TEM was used to determine if the heat induced degradation process of Ni-Fe LDH platelets is dependent on platelet size and/or elemental composition. Upon heating, both a morphological and crystallographic change was evidenced. Surface alterations and changes to the hexagonal morphology are noted as the temperature increases. Material seems to concentrate in spherical modules

the sample. It is important to note that even after heating to 850 °C the SAED pattern retains some features of the parent structure. This implies either that certain platelets remain unperturbed by the increased temperature or that the structure is not wholly degraded.

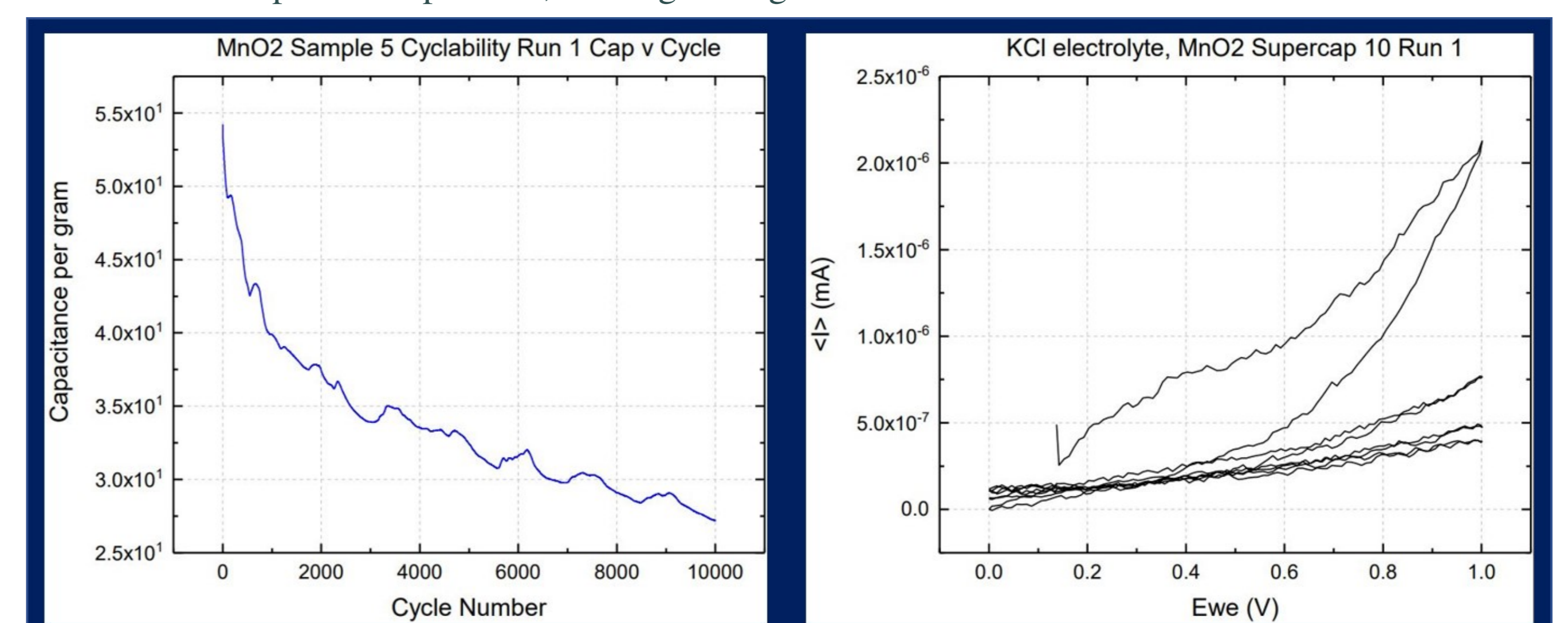


**Figure 1:** a-d; Bright Field Transmission Electron Microscopy (BFTEM) images of micron-sized Ni-Fe LDH hexagonal platelets. The images show the progression of the degradation process at successively higher temperatures. e-h; Selected Area Electron Diffraction (SAED) patterns, corresponding to the arrangements shown a-d, provide information on the integrity and uniformity of the platelet crystal structure.

### 0.6 Analysis of supercapacitors

As previously mentioned, the life-span of energy storage devices is of great interest. The cyclability, or how well the device maintains its electrochemical performance over uses, is a useful tool to measure this property. Here, the MnO<sub>2</sub>-graphene device becomes unusable after roughly 10,000 cycles. It was found that the LiCl PVA gel-electrolyte best preserved the device’s performance over successive runs.

Cyclic Voltammetry that reveals pseudocapacitive activity has a characteristic rectangular-like shape typical indicative of the existence of resistive behaviour only to a point. Here, the quasi-rectangular shape and redox-type peaks indicate sub-optimal performance of the supercapacitor when used in conjunction with a KCl gel-electrolyte. Acid-based gel-electrolytes were found to be inappropriate for use with the printed capacitors, causing damage.



**Figure 2:** A; The decrease in capacitance per gram of the pseudocapacitor, with each successive cycle, is here shown. An ideal device would have invariable capacitance and would retain its efficiency over many cycles. Cyclability is a direct measure of the device’s lifespan. B; The average current through the capacitor is plotted against a varying voltage. Note that the rectangular shape of the graph collapses after the first cycle.

## Conclusions

- Aberration corrected electron microscopy was successfully employed to characterise two-dimensional nanomaterials, determining their structural features and elemental compositions.
- Ni-Fe LDH hexagonal undergo crystallographic morphology at high temperatures leading to the formation of new planes and concentration of the material into spherical particles, first evolved at 450 °C and assuming a random distribution across the hexagonal platelet.
- The electrochemical properties of MnO<sub>2</sub>-graphene devices can be optimised by certain gel-electrolytes. The application of PVA-based electrolytes (with chloride salt ion sources), gave rise to measurable pseudocapacitance in cyclic voltammetry electrochemical characterisation.

## References

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