

ENG8 Report
Examination of Nickel and Aluminium Electrodes
under Plasma Exposure:
A Raman Analysis

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This document contains a Raman analysis of two sets of samples: one Aluminium ring sample (containing reacted and non-reacted zones) and two Nickel rod samples (one pristine sample and one sample after plasma reaction). All samples were measured with a CW laser (central wavelength at 785 nm) and power of 0.2 mW.

1. Samples and Raman spectra

Raman spectroscopy is typically used to determine vibrational modes of molecules. It is commonly used to provide a structural fingerprint by which molecules can be identified. A source of monochromatic light, usually from a laser, is used. The laser light interacts with molecular vibrations, phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the vibrational modes in the system.

Two sets of samples were analysed:

- One Aluminium ring sample containing un-reacted and reacted zones, i.e. white and black areas (measurements performed in both areas)

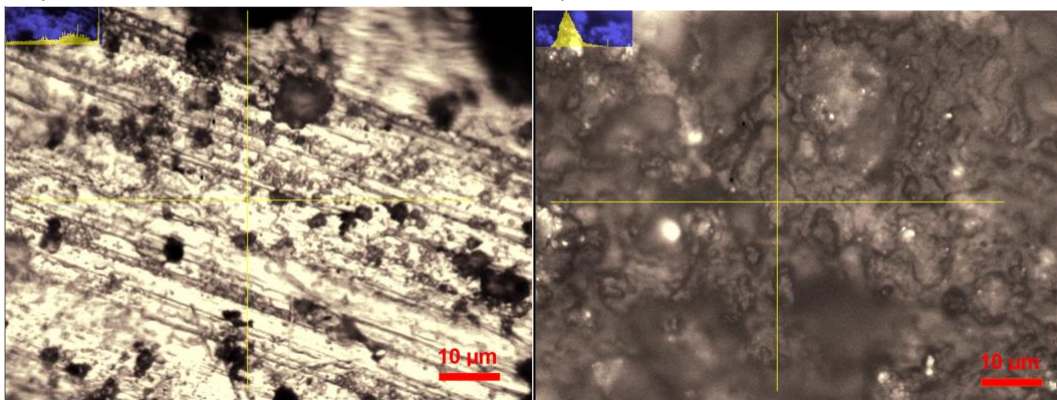


Figure 1: View on microscope objective on aluminium (left) white and (right) black area.

- Two Nickel rod samples: one pristine sample (reference) and one sample after plasma reaction

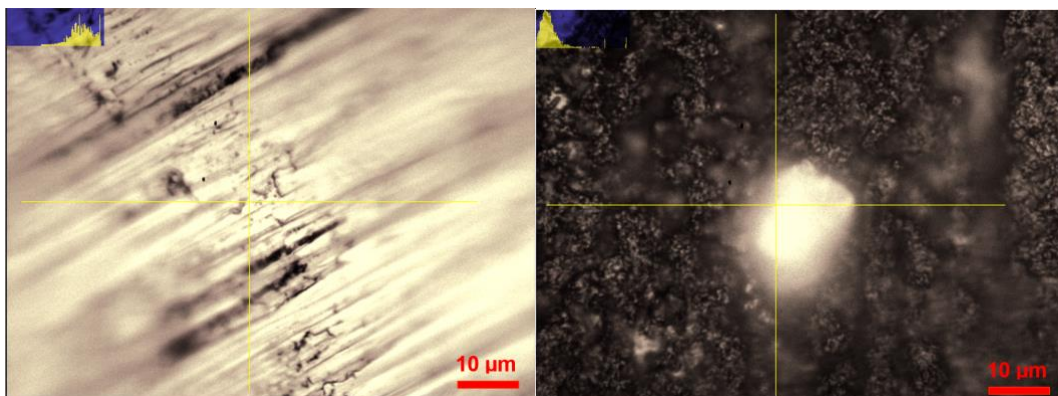


Figure 2: View on microscope objective on Nickel (left) reference and (right) object on post-plasma samples.

All samples were measured with a laser with central wavelength at 785 nm and power of 0.2 mW. The 785nm laser wavelength was needed to reduce some photoluminescence present

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when using more energetic (i.e. 633nm) excitation laser. This resulted in a lower Raman signal, due to lower detection efficiency of the system in the IR frequency range. Therefore, longer integration times were needed to reduce signal noise. Each plotted curve shown in this report is the average of 3 Raman spectra. Each spectrum is measured with 300 seconds integration time. We plot Raman data (after removing background) below.

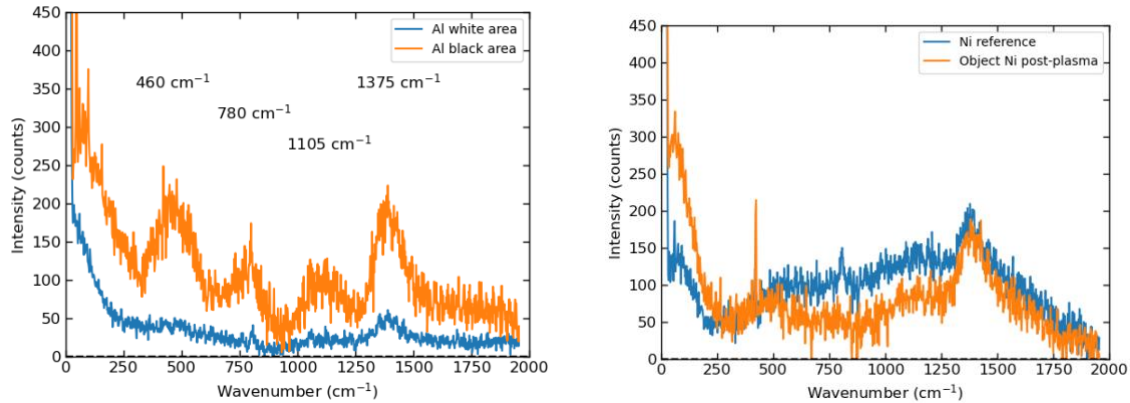


Figure 3: Raman spectra of (left) Aluminium sample on white (blue) and black (orange) areas and (right) Nickel reference (blue) and of an object on Nickel sample after plasma reaction (orange). Sharp peak at 420 cm⁻¹ region is scattered room light, present due to long integration time.

2. Peaks analysis

2.1 Both aluminium and nickel samples

For both analysed cells, we could discard the presence of Cl₂ (ref: 10.1063/1.4942109) as discussion of this molecule was present in other previous reports that might be of interest.

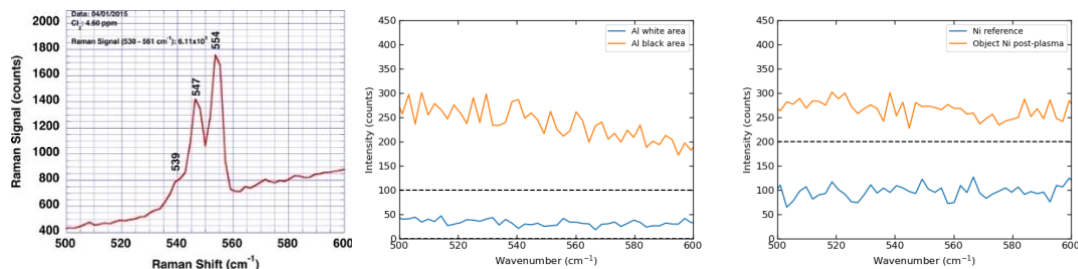


Figure 4: No presence of Cl₂. Raman data from (a) ref 10.1063/1.4942109, (b) Aluminum EnergyCell, (c) Nickel EnergyCell

Amorphous carbon (ref: 10.1515/msp-2015-0067) was another material of interest for this analysis, which we had been asked to focus on. Raman spectrum of amorphous carbon phase is composed of two peaks: the first one in the range of 1320 to 1360 cm⁻¹, called D-band, and the second peak ranging from 1500 to 1600 cm⁻¹, called G-band. Both D and G line appear from sp² hy-bridized carbon structure. The "D" peak corresponds to atoms moving in radial directions in the plane of the graphitic sheet, similar to the breathing mode in benzene. The "D", disorder peak, appears as a result of dislocations in the lattice, deriving its name from the

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fact that they are “disorder-induced modes”. The “G” peak corresponds to neighboring atoms moving in opposite directions perpendicular to the plane of the graphitic sheet. The relative intensities of these vibrations vary a lot depending on the crystallinity. The structures of amorphous carbon phases depend on synthesis conditions and are reflected in their Raman spectra, i.e. the positions of D ($\sim 1375\text{ cm}^{-1}$) and G lines ($\sim 1575\text{ cm}^{-1}$) - fig.7 a. The excitation laser for Raman detection can also modify the exact position of the Raman peaks, with the 785nm excitation laser determining a broadening and merging of the D and G peaks (fig.7b).

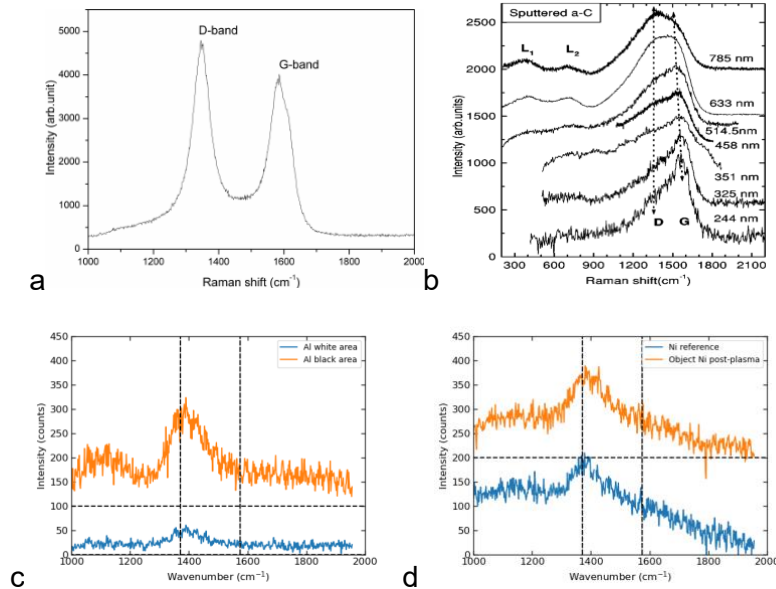


Figure 7: (a,b) Data from reference 10.1515/msp-2015-0067 and 10.1103/PhysRevB.64.075414. (c,d) Aluminium and Nickel EnergyCells measured data. Horizontal black dashed line marks the zero position for the orange curves. Vertical black dashed line marks the position of 1375 cm^{-1} and 1575 cm^{-1}

When focusing in the $1000\text{-}2000\text{ cm}^{-1}$ range, we could observe (for both Ni and Al electrodes) a peak at 1370 cm^{-1} (possibly linked to D-band), while the G-band peak at 1575 cm^{-1} might fall under the tail of the D band, as it happens when a 785 nm excitation laser is used (fig 7b). Peak at 1370 cm^{-1} therefore might suggest carbon is presence in all samples, both in reacted and unreacted areas. In the Al sample, the intensity of the 1370 cm^{-1} is four times stronger in the reacted sample compared to the unreacted one, suggesting more material being present in the reacted area.

2.2 Nickel samples

In the Nickel electrode two main peaks could be observed. On top of the 1375 cm^{-1} peak discussed in section 2.1, hinting to presence of amorphous carbon (before and after plasma reaction), a second peak at lower wavenumbers could be identified ($\sim 490\text{ cm}^{-1}$) after plasma reaction. Nickel oxides (NiO/Ni₂O₃ - ref: 10.1080/01932691.2020.1814804) can be identified with this peak, suggesting NiO is created with plasma reaction.

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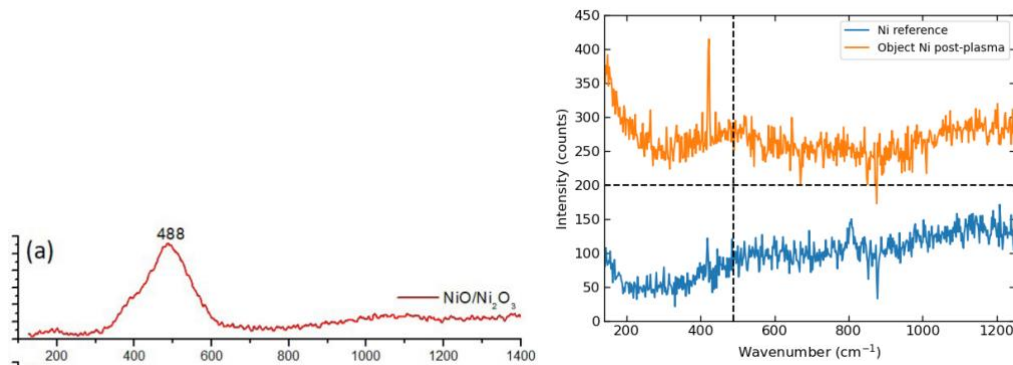


Figure 8: Shallow peak at 488 cm^{-1} region (vertical dashed black line) can be of the NiO/Ni₂O₃. Horizontal black dashed line marks the zero position for the orange curves.

2.3 Aluminium sample

In the Al sample, on top of the 1375 cm^{-1} peak discussed in section 2.1, hinting to presence of amorphous carbon (reacted and un-reacted areas), we could see three additional Raman peaks around 460 cm^{-1} , 780 cm^{-1} , 1105 cm^{-1} in the reacted area (black) of the Al electrode.

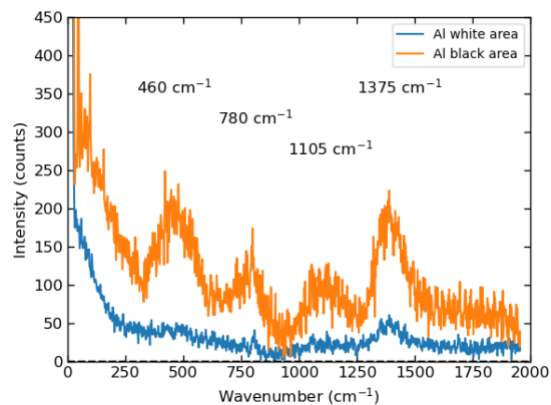


Figure 9: Raman data on EnergyCell. Raman peaks are visible around 460 cm^{-1} , 780 cm^{-1} , 1105 cm^{-1} and 1375 cm^{-1} in the reacted area of the sample (orange) and only one peak at 1375 cm^{-1} in the un-reacted area of the sample (blue).

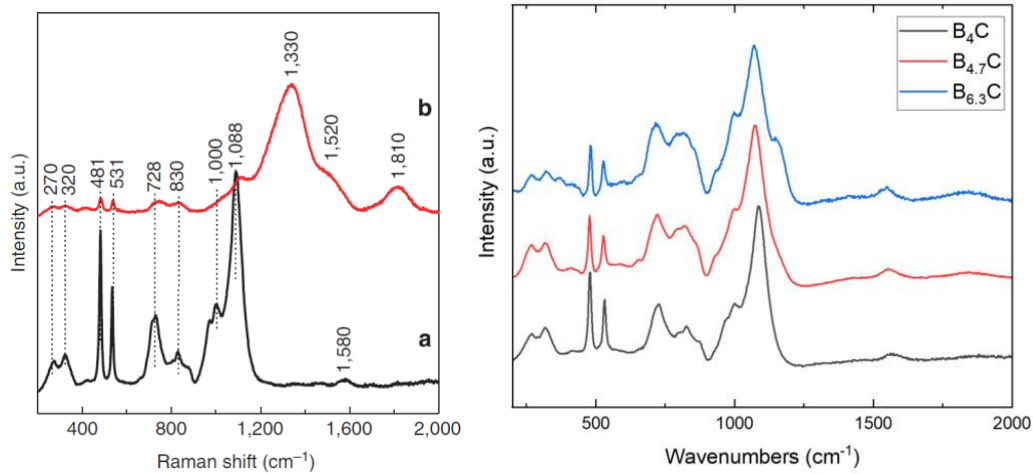


Figure 10: (Left) Data from ref 10.1038/ncomms3483 showing the peaks of crystalline B_4C (a), with peaks at 728, 830, 1000 and 1088 cm^{-1} , and of amorphous B_4C (b), with peaks at 1330, 1520 and 1810 cm^{-1} . Vertical dashed lines mark the positions of (from left to right) 728, 830, 1000, 1088, 1330, 1520 and 1810 cm^{-1} . (Right) Data from ref 10.3390/ceramics3030027 showing peaks of B_4C , $B_{4.7}C$, and $B_{6.3}C$. Broad peaks are visible ~ 1100 and $750 cm^{-1}$, and multiple peaks around $500 cm^{-1}$ region.

Given the functioning of the EnergyCell, presence of Boron has been suggested as a possible source of Raman signal, therefore we checked against boron carbide compounds. From literature, boron carbide compounds (reference for B_4C : 10.1038/ncomms3483 and 10.3390/ceramics3030027) generate broad peaks below $1200 cm^{-1}$ region (Fig. 10). Their intensity and sharpness are related to the crystallinity of the material, leading to a significant sample-to-sample variation of the boron carbide compounds Raman signature. From ref. 10.1038/ncomms3483 and 10.3390/ceramics3030027 we can see similarities between boron carbide compounds Raman peaks, specifically with multiple peaks around $500 cm^{-1}$ region and broad peaks $\sim 750 cm^{-1}$ and $\sim 1100 cm^{-1}$, and the measured broad peaks around $460 cm^{-1}$, $780 cm^{-1}$, $1105 cm^{-1}$. It must be noted that signal is low, due to the need of 785nm laser and a probably not abundant amount of material on the electrode. This determined a noisy Raman signal, hence a poor determination of clean shape of the Raman peaks. For this reason, although the measured broad peaks around $460 cm^{-1}$, $780 cm^{-1}$, $1105 cm^{-1}$ might hint to the possible presence of boron carbide compounds, we cannot exclude that other compounds might have determined similar peaks.

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