Proceedings of the 6th International Conference on Theoretical and Applied Nanoscience and Nanotechnology (TANN'22)
Niagara Falls, Canada – June 02-04, 2022
Paper No. 139
DOI: 10.11159/tann22.139

Formation of NiO Thin-Film via Picosecond Laser Pulses for Energy Storage Electrode Fabrication

Mayuresh Khot, Amirkianoosh Kiani
[1]Ontario Tech University
200 Simcoe St N, Oshawa, ON L1G 0C5
mayuresh.khot@gmail.com; Amirkianoosh.kiani@ontariotechu.net

***Abstract* –** Consumer demand in portable and mobile electronics has noticed exponential rise leading to increases demand for energy storage devices. Once such device is supercapacitor which relies on interfacial, surface charge storage. With increased surface area, better capacitance is observed with assistance of nanoengineering. In this paper, a thin oxide layer is generated on Ni sheet surface with ultra-short pulses for laser ablation of Ni. The effects of power were analysed by keeping other parameters such as pulse duration, frequency, and irradiation scan speed constant. The 3D nanostructures of metal oxide exhibited pseudocapacitive behaviour. The nanostructured oxide layer assisted in better ion diffusion and ion adsorption and desorption as observed by the electrochemical tests performed. The paper promotes synthesis of nanoparticles (NPs) with green approach such as laser ablation as part of future manufacturing methods for electrode fabrication

***Keywords*:** Psuedocapacitance, Transition Metal Oxides, Laser Pulse Ablation, Electrodes, Nano particles, Energy storage devices

1. Introduction

Undoutedly, the vast growth in technology in past few decades has influenced many consumers around the world to purchase advanced electronics making life much more simplistic. The main element of these electronics are energy storage devices which simply provide electronics the dense energy or power required to operate over a period. Traditional capacitors and batteries are discussed quiet often when it comes to energy storage systems, however, one shines where the other is weakest and vice-versa. The energy storage system (ESS) that bridges the gap between the two are supercapacitors or also known as ultracapacitors[1]. Supercapacitor's work based on surface charge storage of ions from electrolyte solutions onto the electrode surface, therefore, electrode with excellent surface area is most desired[2]. Compared to traditional capacitor, supercapacitors make use of electrolyte-soaked separator compared to polarized dielectric. On the other hand, unlike batteries, supercapacitors go under rapid reversible reactions without any crystallographic phase transition[3]. Supercapacitors possess some desirable characteristics such as fast charging-discharging, excellent cyclability, easy manufacturing, equally dense power density and energy density[4]. Supercapacitors can be classified in three EES, the first is electric double layer capacitor (EDLC) which stores charge electrostatically upon polarized terminal. The EDL strengthens as the voltage is ramped up leading to greater ion adsorption-desorption occurring at the electrode-electrolyte interface leading to charge storage. EDLCs however are restricted or limited to only carbon-based material such as activated carbon, carbon nanotubes, graphene etc. The second type of supercapacitor is the pseudocapacitor whose working principle solely depends upon the quick, reversible redox reactions occurring at the oxide layer at the surface. Psuedocapacitors hold charge one order greater than EDLC due to the added surface redox reactions with conjunction of EDL charge storage. Transition metals and conducting polymers are preferrable used however transition metals are mainly focused due to their abundance, excellent chemical stability, several interchangeable oxidation couples, and simple synthesis process. The third type of supercapacitor is hybrid capacitor which makes use of one electrode as EDLC and the other electrode as pseudocapacitance influencing electrode. In this paper, pseudocapacitors electrode made from metal oxide is analysed[5, 6].

The electrode in pseudocapacitor plays the most essential role as discussed before, specifically electrodes with magnificent surface area for maximum ion electro sorption and more provision of active sites for redox reaction. This can be attained by nanoengineering the active material allowing more surface to volume ratio. Desired design of the nanostructure material yields uniformly distributed porous structure, maximum ion diffusion channels and lower impedance. There are many ways to synthesize NPs of metal oxides such as sol-gel, chemical vapor deposition, hydrothermal/solvothermal, pyrolysis, electrospinning, electrodeposition, pulsed laser deposition, magnetron sputtering, laser ablation and many more. There are several drawbacks to many of the synthesis processes such as post treatment, multi-step, harmful chemical environment, and time-consuming process. In this paper, simple irradiation of Ni, a transition metal is oxidized via ultra-short pulse laser in ambient temperature and pressure to develop 3D nanostructures resulting in formation of pseudocapacitance[7].

2. Experimental

Irradiation of Ni sheet was carried out on Ni to form NiO. The effects of power were analysed with the pulse duration, frequency and irradiation scan speed kept constant

2.1. Experimental Setup

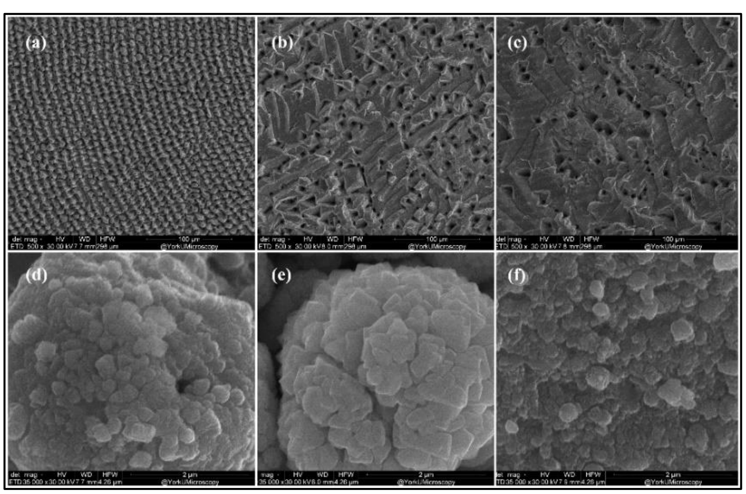
Ni sheet of 0.3 mm thickness was acquired from Sigma Aldrich. The Ni sheet was cleaned with acetone and Di water thoroughly to remove any manufacturing or packaging residue. The Ni sheet was irradiated with laser as seen in Table 1. The acquired oxidized samples were then used in a 3-electrode setup to conduct electrochemical tests. 6M KOH was used as aqueous alkaline electrolytic solution for the experiment and mercury/mercury-oxide reference electrode was used due to acceptance tolerance of high Ph from alkaline solution. Platinum wire was used as counter electrode. The tests were conducted with help of SP-150 biologic potentiostat and EC-lab software.

Table 1: Laser parameters for in-air laser ablation.

Samples	Parameters			
	Power (W)	Frequency (kHz)	Pulse Duration (ms)	Scan Speed (mm s^{-1})
P1	5	1200	150	50
P2	10	1200	150	50
P3	15	1200	150	50

2.2. Material Characterization

The samples acquired were inspected under SEM to understand the surface morphology of the structure. Starting from Fig. 1a, at lower magnification, the surface was observed to be evenly distributed porous structure. Fig. 1b, on the other hand demonstrated slightly less uniformity and porous structure. Lastly Fig. 1c, shows deep valleys and craters



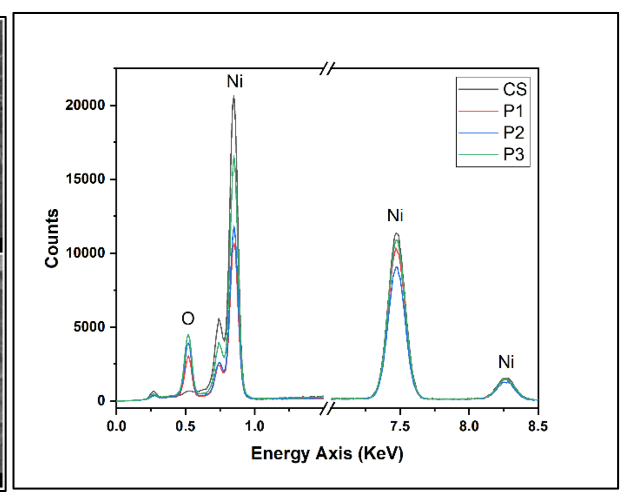


Fig 1 (a-e) Lower magnification of samples showing uniformity of strucutre on macroscale. (d-f) At higher magnification nanostrucutres are observed (g) the EDX demonstrates the tracing of O confirming formation of oxide layer

along with small micro cracks running throughout the structure. On the other hand, at higher magnification, Fig. 1d, demonstrates micro sized spherical growth. Fig. 1e, shows crystal structure formation on the sphere and lastly Fig. 1f shows nanosized dots on the surface, like Fig. 1d but slightly smaller in scale. The EDX was conducted on the samples which indicated presence of O due to formation of oxide layer. Compared to P2 and P3, P1 had smaller O detection but interestingly, Ni had less detection for P1

2.3. Results and Discussion

Samples obtained with conformance of parameters in Table 1 underwent electrochemical tests such as cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS) as shown in Fig 2a-c. Fig a is a CV of NiO which shows faradaic dominant redox peaks and the behaviour of the samples during oxidation and reduction process. P1 shows best CV characteristics due to excellent current density and charge storage. This is probably due to the uniformly distributed 3D nanostructures allowing to form abundant active sites and electro sorption. The GCD

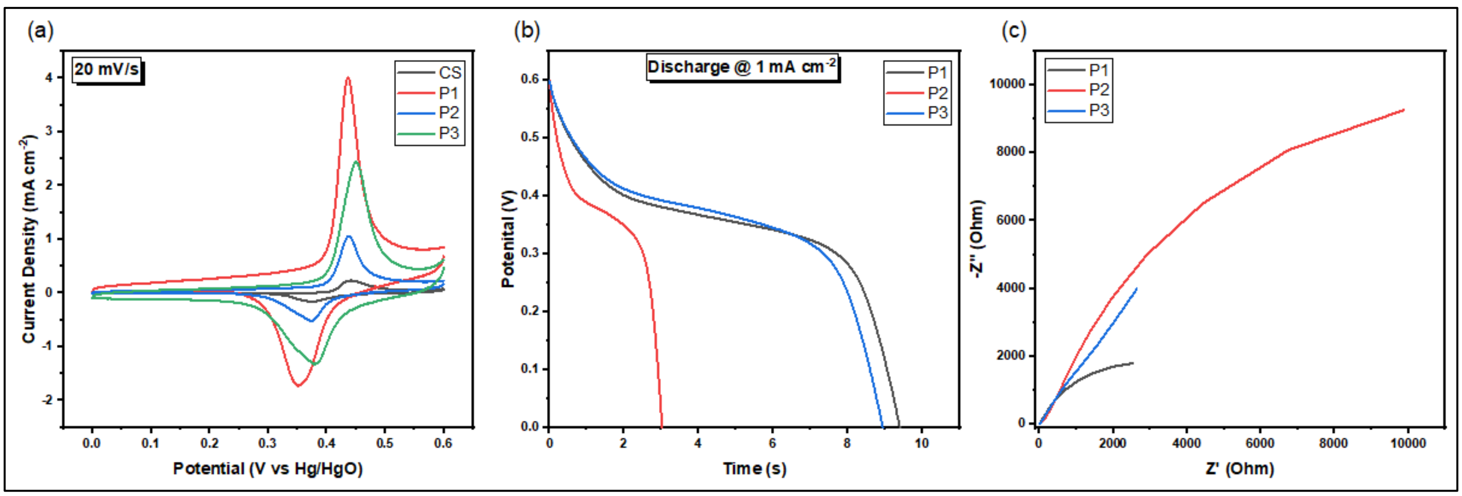


Fig. 1: a) The CV curve shows P1 having the highest charge storage along with high reversibility. (b) The discharge curve of P1 lasts longer indicating more charge was stored in P1 sample. (c) The EIS curve illustrating P1 having least of the impedance due to its uniform structure proving better electrochemical interaction.

curve which demonstrates the time required to store charge up to stable potential is displayed in Fig 2b, P1 has noticeably more charge storage as more time is taken to deplete the charge from the device, P2 demonstrated worst performance. This is potentially due to less exposed surface area conforming the results obtained from SEM images. EIS once again, proves the results from CV and GCD. As can be observed, the higher, extended impedance curve of P2 shows its poor performance, whereas P1 has minimal extension, therefore demonstrating minimal impedance of the samples

3. Conclusion

The study of power for laser ablation of transition metal to form metal oxide was observed. The obtained metal oxide or NiO was to be tested for pseudocapacitive application in psuedocapacitors. The lower power demonstrated a uniformly distributed, self-standing nanostructures which resulted in the best performance compared to other samples. The higher power samples were lacking the uniform distributed surface area resulting in poor electrochemical performance. Laser ablation is a simple technique to synthesis self-standing nanostructures which are considered “green” method of fabrication due to its one step, direct synthesis of Nanostructures for transition metals to be used in energy storage devices

Acknowledgements

This research was funded by the Natural Sciences and Engineering Research Council of Canada (NSERC).

References

[1] Pech D, Brunet M, Durou H, Huang P, Mochalin V, Gogotsi Y, Taberna PL, Simon P., "Ultrahigh-power micrometre-sized supercapacitors based on onion-like carbon," Nature nanotechnology, vol. 5, no. 9, pp. 651-654, 2010.

[2] L. L. Zhang and X. Zhao, "Carbon-based materials as supercapacitor electrodes," Chemical Society Reviews, vol. 38, no. 9, pp. 2520-2531, 2009.

[3] J. Xie, P. Yang, Y. Wang, T. Qi, Y. Lei, and C. M. Li, "Puzzles and confusions in supercapacitor and battery: Theory and solutions," Journal of Power Sources, vol. 401, pp. 213-223, 2018.

[4] J. Zhu, D. Yang, Z. Yin, Q. Yan, and H. Zhang, "Graphene and graphene-based materials for energy storage applications," Small, vol. 10, no. 17, pp. 3480-3498, 2014.

[5] M. Vangari, T. Pryor, and L. Jiang, "Supercapacitors: review of materials and fabrication methods," Journal of energy engineering, vol. 139, no. 2, pp. 72-79, 2013.

[6] H. Xia, J. Feng, H. Wang, M. O. Lai, and L. Lu, "MnO2 nanotube and nanowire arrays by electrochemical deposition for supercapacitors," Journal of Power Sources, vol. 195, no. 13, pp. 4410-4413, 2010.

[7] A. Gholami, C.-H. Yim, and A. Kiani, "Electrochemical Performance of Titania 3D Nanonetwork Electrodes Induced by Pulse Ionization at Varied Pulse Repetitions," Nanomaterials, vol. 11, no. 5, p. 1062, 2021.