



Electrochemical performance of laser micro-structured nickel oxyhydroxide cathodes



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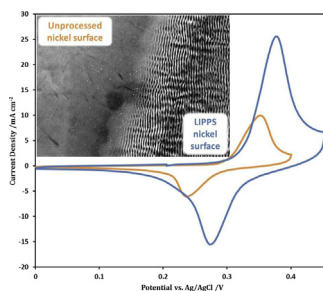
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HIGHLIGHTS

- The surface of Ni foils was processed by ultra-short pulse length, low energy laser light.
- The technique produced periodic ripple micro-structures (LIPPS) at the surface of the Ni.
- LIPPS yields an increased electrochemical activity relative to unprocessed planar Ni by a factor of 2.5.
- LIPPS electrode modification could be relevant for Ni based micro-battery systems.

GRAPHICAL ABSTRACT



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ABSTRACT

This study describes the preparation and analysis of laser micro-structured nickel metal electrodes for application as a cathode material in micro-batteries based on the nickel oxyhydroxide chemistry. Using ultra-short pulse length lasers (picoseconds to femtoseconds); surface micro-structures in the form of ripples are rapidly generated at the surface of nickel metal cathodes. These ripple micro-structures, with a periodic spacing approximately equal to the wavelength of laser radiation used, are more commonly referred to as laser-induced periodic plasmonic structures (LIPPS). The electrochemical activity of the LIPPS nickel metal cathodes is investigated in aqueous KOH using cyclic voltammetry. Across a wide range of scan rates, the results of the voltammetry show that the formation of LIPPS yields a considerable enhancement in the electrochemical activity of the nickel surface. The observed enhancement is attributed to both the greater surface area of the rippled surface relative to a planar nickel surface and a thicker NiO_x layer generated by the laser process.

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1. Introduction

Nickel is a widely used electrode material in battery technologies (e.g. nickel/cadmium, nickel/metal hydride, nickel/hydrogen,

nickel/zinc, nickel/iron) [1]. Secondary battery technologies utilising a nickel cathode material and an alkaline electrolyte have nickel hydroxide, Ni(OH)₂ as the electrochemically active material. During charge/discharge electrode cycling, Ni(OH)₂ undergoes reversible oxidation to form the charged-state material, nickel oxyhydroxide, NiOOH. The ability of a nickel-based energy storage device to store and deliver power relies on the amount of the electrochemically active material that can accumulate at the electrode/electrolyte interface. It would be expected that maximising the accessible

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surface area of nickel cathodes would create a larger area for active material accumulation, leading to improved energy storage performance.

Efforts to improve the performance of nickel electrodes by maximising surface area have, so far, primarily involved the use of templating. Various techniques have been used to create templates onto which the electrode material can be deposited and, in some cases, the template can be subsequently removed, thus creating a nickel cathode framework. The template methods used so far include using; the micropores of an high internal phase emulsion polymer [2–4], the aqueous domains of a self-assembled liquid crystal template [5,6], the self-assembly of a mutant Tobacco mosaic virus to a gold surface [7,8] and a self-assembled opal template of 1.8 μm polystyrene spheres [9].

This work presents laser micro-structuring of nickel surfaces as an alternative to template-directed preparation. It has been shown previously that the surface of nickel metal, as well as other metals and semiconductors, can be rapidly modified with the use of ultrashort laser pulses [10–21]. The particular process of interest is the formation of laser-induced periodic plasmonic structures (LIPPS). These structures exist in the form of ripples at the solid surface and were first observed during the examination of semiconductor surface damage by a ruby laser [10].

It was initially proposed that the formation of LIPPS was a result of interference between the surface scattered wave and the incident laser radiation resulting in periodic spacings approximately equal to the laser wavelength [11,12]. This concept has been developed further based on the assumption that the formation of LIPPS occurs as a result of inhomogeneous energy deposition just beneath the surface [22,23]. Furthermore, some recent studies have also provided evidence to suggest that interference between the incident laser and excited surface plasmons may also contribute to the formation of LIPPS [13,15,19]. The ripples that result from the surface laser treatment form perpendicular to the direction of the lasers polarisation.

The formation of micro-structures at the nickel surface can be achieved extremely rapidly by laser-treatment (dependent on parameters and setup, typically 4 cm^2 per second is possible), removing the need for any complex or time-consuming synthesis steps required during templating. In particular, the treatment with ultrashort laser pulses to yield high surface area nickel electrodes could create materials for possible applications in micro-batteries. The nickel hydroxide/oxyhydroxide couple has been previously investigated as a possible micro-battery electrode in several different forms in addition to the previously described templating methods; thick-film printed electrodes using a mixture of nickel hydroxide, fine nickel metal powders and binder material as the ink [24], high-aspect ratio pillar nickel electrodes [25], hierarchical micro-spheres and micro-flowers of $\text{Ni}(\text{OH})_2$ [26] and graphene encapsulated nickel core-shell electrodes [27].

2. Experimental

2.1. Laser micro-structuring of nickel foils

High-purity nickel foils with a thickness of 1.0 μm (Goodfellow) were used in the preparation of the nickel electrodes. From a thin strip of nickel (ca. 25 \times 8 mm) an area of 5 mm^2 was treated using ultra-short pulse length (femtosecond and picosecond) and low pulse energy (1–3 μJ per pulse) lasers. Two laser systems were used in this study; an amplified Ti:Sapphire laser (Clark-MXR CPA2010) and a custom made Nd:VAN seeded regenerative amplifier laser (High-Q IC-355-800 ps). The Clark-MXR laser system has a pulse length of 160 fs, a repetition rate of 1 kHz and a central wavelength of 775 nm, with a similar set-up to that detailed in Ref. [28]. The

High-Q laser is a 10 ps pulse length laser system capable of repetition rates up to 50 kHz and output wavelengths of 1064 nm, 532 nm and 355 nm (355 nm wavelength pulses have not been used in this work). The overall set-up for the High-Q laser system is the same as detailed in Ref. [29]. Both set-ups used a scan head and f theta lens to deliver the laser beam to the work piece. All experiments described in this study used linearly polarised laser pulses. Samples were processed with the laser beam at a normal incident angle as the structure of LIPSS produced can be sensitive to this incident angle.

The laser spot was scanned across the planar nickel surface in parallel lines at a predefined scan rate (mm s^{-1}). The overall laser fluence (energy delivered per unit area) was controlled by varying parameters of the laser treatment; repetition rate, pulse intensity, diameter of the laser spot, the number of overlapping scans and the hatch distance (separation between the parallel scans).

2.2. Characterisation of nickel surfaces

The formation of the LIPPS at the nickel surface was characterised by scanning electron microscopy (SEM) and white-light interferometry. White-light interferometry measurements were completed on a WYKO NT1100 Optical Profiling System. SEM imaging was performed on a JEOL JSM-6610 instrument working at 30 keV.

2.3. Electrochemical analysis of laser-processed nickel

Electrochemical measurements were obtained using a standard three-electrode cell equipped with the nickel working electrode, a platinum wire counter electrode and a silver/silver chloride reference electrode. A 3 M KOH solution in distilled water was used as the electrolyte. All voltammetric measurements were conducted using a Bio-Logic VSP potentiostat at room temperature. To prepare the processed nickel foils for testing, the unprocessed nickel surface was coated in a few layers of insulating acrylic lacquer to create an exposed, well-defined geometric area of purely laser-processed nickel metal. A platinum wire was attached to the nickel using silver conducting paste to ensure a good electrical contact. The nickel strip was washed in a small amount of additional 3 M KOH electrolyte solution prior to immersion into the electrolyte.

Cyclic voltammetry of the different nickel samples was performed in a potential range of 0–0.45 V vs. Ag/AgCl to study the oxidation/reduction peaks of the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ couple. The nickel was cycled at a range of scan rates from 10 mV s^{-1} to 2500 mV s^{-1} . These measurements were compared with control samples of unprocessed nickel metal foil.

2.4. Surface characterisation of the laser processed nickel

Raman spectra were recorded with a Raman microscope (Renishaw inVia), using a 633 nm wavelength laser focussed through an upright microscope (Leica), via a 50 \times objective (Leica). X-ray photoelectron (XPS) experiments were performed in a standard ultrahigh vacuum surface science chamber consisting of a PSP Vacuum Technology electron energy analyser (angle integrating $\pm 10^\circ$) and a dual anode X-ray source. [30] The base pressure of the system was less than 2×10^{-10} mbar, with hydrogen as the main residual gas in the chamber. The XPS measurements were carried out with a Mg K-alpha source (1253.6 eV). The spectrometer was calibrated using Au 4f_{7/2} at 83.9 eV. The samples were corrected for charging using the adventitious carbon 1s peak.

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