



Synthesis and characterization of 3D Ni nanoparticle/carbon nanotube cathodes for hydrogen evolution in alkaline electrolyte



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HIGHLIGHTS

- Ni NPs were deposited onto MWCNTs in a single step dry process.
- The electrocatalytic activity of Ni NP/MWCNT in terms of hydrogen evolution is dependent on the NP loading.
- The Ni NP/MWCNT electrocatalysts show a significant increase in electrocatalytic activity relative to a bulk Ni plate.

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ABSTRACT

Renewable alternative energy sources are required to decrease or eliminate the use of environmentally unfriendly fossil fuels. Hydrogen produced by electrolysis has been identified as one such renewable energy carrier. In the current work, Ni nanoparticle (NP)-decorated multiwall carbon nanotube (MWCNT) electrocatalyst cathodes are prepared by a simple two-step procedure. MWCNTs are grown on stainless steel meshes by thermal-chemical vapour deposition (t-CVD) and then decorated with Ni NPs by pulsed laser ablation (PLA). The morphological and electrochemical properties of the produced Ni NP/MWCNT cathodes were characterized through electron microscopy and linear Tafel polarization (LTP)/electrochemical impedance spectroscopy (EIS), respectively. SEM and TEM imaging revealed that the Ni NPs deposited by PLA are on the order of 4 nm in diameter with a narrow size distribution. The LTP measurements showed that the electrocatalytic activity of the Ni NP/MWCNT cathodes towards the hydrogen evolution reaction (HER) is dependent on PLA time and shows a maximum at $t_{PLA} = 40$ min. EIS measurements revealed that the HER response is characterized by a two time constants process representing HER kinetics and adsorption of hydrogen.

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1. Introduction

It has been established that energy consumption increases with global development. However, traditional fossil-based fuels may be insufficient to meet the need due to their finite supply. Hydrogen has been identified as a clean energy fuel carrier; as the most abundant element on Earth, hydrogen is truly renewable and has a large energy storage potential [1–3]. For these reasons, hydrogen has been referred to as the “fuel of the future”.

Electrolysis in alkaline media has been used for a number of years to electrochemically generate hydrogen [4–7]. Electrolysis

also offers high purity (near 100%) hydrogen production for a modest energy input [5]. However, alkaline electrolyzers have some disadvantages that must be considered, such as the use of very alkaline electrolyte (30 wt.% KOH), large system size, and large total cell operating potential due to the presence of various ohmic drops in the cell (including those related to the electrode reaction kinetics) [6,8]. Despite these shortcomings, there has been a renewed interest in alkaline electrolysis [9]. The current work addresses the latter issue, and more specifically, it focuses on the improvement of the hydrogen evolution reaction kinetics.

Electrocatalysts (cathodes) for hydrogen generation typically consist of a metal electrode supported on an inert conductive support. The best hydrogen generating metals are noble metals (Pt, Ru, Ir). This is a direct consequence of the intermediate M–H_{ads} bond strength in the hydrogen evolution reaction (HER) [10,11]. In alkaline electrolyzers, non-noble metal electrocatalysts are used to

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circumvent the use of expensive noble metals. Unfortunately, two major drawbacks are associated with the use of non-noble metal cathodes in alkaline electrolyzers: (i) operation at a large overpotential due to the poor electrocatalytic properties of the cathode material relative to noble metals and (ii) the bulkiness of the system due to the requirement for a large surface area to generate sufficient amounts of hydrogen. Of the non-noble metals, nickel has been identified as a good candidate electrocatalyst material due to its low cost and relatively large electrocatalytic activity [12,13]. Two main approaches for the improvements of the electrocatalytic activity of Ni have been applied: (i) modification of its intrinsic (material-related property) [8,14–16] and (ii) extrinsic (surface area-related property) [14–20] electrocatalytic activities. The current work focuses on (ii).

Numerous attempts have been made to modify the extrinsic factors associated with the HER on Ni electrodes. In a recent study by Lahiri et al., an electrodeposited microporous Ni film was used as a dual-use HER and hydrogen storage (through the formation of nickel hydrides) electrode in an ionic liquid electrolyte [21]. Further, Döner et al. have recently shown that non-noble transition metals (Ni, Co, and their alloy) can be electrodeposited onto carbon felt to produce porous metal coatings on a large area support which yields very effective HER electrocatalysts in alkaline media [22]. For the case of the Ni–Co alloy, a measure of the electrocatalyst's intrinsic electrocatalytic activity was studied as well. Unsupported Ni powders have also been suggested as an alternative to Pt electrocatalysts in electrochemical hydrogen pumps [23]. These Ni nanomaterial studies are not limited to 2D electrodes. Yang et al. have recently reported a 3D electrode material using boron-doped diamond nanowires locally tipped with Ni nanoparticles for generic use as HER and glucose oxidation electrodes in alkaline electrolyte [24]. Clearly, Ni is an attractive alternative for reducing the cost of hydrogen generating technologies.

Much attention has recently been given to nanomaterials for a myriad of applications. One of the first major breakthroughs in nanomaterial synthesis originated from the discovery of carbon nanotubes (CNTs) by Iijima [25]. Since their discovery, CNTs have seen wide-spread use in many fields, including alternative energy, medicine, and nanofluid development, to name but a few [26–28]. Novel CNT synthesis techniques have recently been developed using thermal-chemical vapour deposition (t-CVD) where multiwall CNTs (MWCNTs) are grown in a single step onto a metal supporting catalyst [28,29]. It has been reported that MWCNT synthesis can be done easily, inexpensively, and readily scaled up using t-CVD [28]. In the t-CVD process developed in our laboratory, the MWCNTs form an open 3D matrix onto which other nanomaterials, such as metal electrocatalyst nanoparticles (NPs), can be readily immobilized [30]. The NP-decorated MWCNTs show a tremendous increase in active surface area on which an electrochemical reaction can be performed.

There are several techniques currently used to synthesize metal nanoparticles including wet chemistry methods as well as dry methods, including cathodic arc erosion, and pulsed laser ablation (PLA) [30–34]. Of these techniques, PLA has been shown to be very effective at synthesizing highly dispersed streams of metal NPs with small diameters, tight size distributions, and without producing significant amounts of micron-sized particles. These properties are very desirable in terms of high-surface area electrocatalyst materials and as such, PLA has been chosen for NP synthesis in the current work.

In this work, the marriage between nanoparticle and nanotube complement each other to produce high-area Ni NP-decorated MWCNT forests on which HER can occur. However, metal nanoparticle immobilization onto MWCNTs is not a new concept. For example, recent studies have shown that it is possible to combine

both using various techniques. Martis et al. were able to synthesize carbon nanotube/Ni nanocrystal composites using electrodeposition [35,36]. However, imaging of the composite readily revealed that the MWCNTs heavily agglomerated and formed a “film” incorporating sparsely distributed Ni particles. It is unknown whether these materials would behave as truly 3D HER electrodes. Further, Zhang et al. have shown that Ni NPs can be immobilized onto MWCNTs by chemical reduction from Ni-containing salt precursors [37]. Others have also shown that it is possible to combine Ni NPs and MWCNTs through chemical reduction [38–40]. Unfortunately, using chemical reduction/electrochemical plating results in either large metal particles or thin Ni films covering the MWCNTs. Both geometries are undesirable for HER; agglomerations of NPs trap evolved hydrogen gas reducing available surface area and the available surface area is not initially maximized, respectively.

What these few examples suggest is that wet chemistry/electrochemistry methods for metal nanoparticle immobilization on MWCNTs are relatively common. However, physical deposition (dry) methods are not encountered as frequently. PLA has been used in the past to immobilize metal nanoparticles on MWCNT surfaces. For example, Mortazavi et al. have synthesized Pd nanoparticle/MWCNT hydrogen storage electrodes in deionized water [41]. It is unclear how much of the MWCNTs were covered with Pd as the MWCNTs were in a fluidized powder form. Because pristine MWCNTs were purchased as a powder, it is unclear what was the degree of MWCNT agglomeration prior to PLA. As a result, it is surmised that only the outer portion of the agglomerates would be covered by nanoparticles. Subsequently, the fabricated hydrogen storage electrodes were dropped onto a graphite plate and dried. It is the authors' opinion that the drying step would cause further agglomeration of the MWCNTs and contribute to a lower overall surface area due to the hydrophobic nature of pristine MWCNTs.

We show that Ni NP/MWCNT electrocatalysts for hydrogen generation can be synthesized easily and efficiently with a great level of control. Using t-CVD and PLA, an effective Ni NP electrocatalyst supported on an open 3D MWCNT matrix grown on an inexpensive porous stainless steel substrate (mesh) was produced in a simple two-step process. The simplicity of the electrode synthesis, the 3D nanostructure of the MWCNTs, and the control of NP deposition (size, absence of agglomeration, etc.) offered by PLA yield marked improvements over (effectively 2D) nanostructured Ni electrocatalysts used in the past. This electrocatalytic nanomaterial offers a marked increase in electrocatalytic activity in the hydrogen evolution reaction (HER) relative to bulk Ni (a 2D Ni plate).

2. Experimental considerations

2.1. MWCNT growth by t-CVD

An established t-CVD technique first developed by Baddour et al. and later modified by Hordy et al. [28,29] was followed to grow MWCNTs for use as electrically-conductive electrocatalyst supports. In this technique, stainless steel (SS) 316 grade mesh discs (400 series, 25 μm grid bar, 1.6 cm dia.; McMaster-Carr, USA) are used as the catalyst/substrate for MWCNT growth. The SS discs are first degreased in acetone for 30 min and then placed in a quartz tube furnace (55 mm i.d.) and heated to 700 $^{\circ}\text{C}$ under flowing Ar ($592 \pm 5 \text{ cm}^3 \text{ min}^{-1}$). Acetylene is used as the carbon source and injected into the furnace for 4 min at a constant flow rate of $68 \pm 5 \text{ cm}^3 \text{ min}^{-1}$ followed by an isothermal growth step of 30 min at 700 $^{\circ}\text{C}$ under Ar ($592 \pm 5 \text{ cm}^3 \text{ min}^{-1}$). Afterwards, the system is allowed to cool down to room temperature (22 $^{\circ}\text{C}$) before removing the MWCNT-covered SS mesh (MWCNT/SS) electrodes from the

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