Electrochemical generation of active coenzyme 1,4-NADH for enzymatic lactic acid production on metal oxides with engineered defects/active sites

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論　文　名：Electrochemical generation of active coenzyme 1,4-NADH for enzymatic lactic acid　production on metal oxides with engineered defects/active sites
(設計された欠陥/活性部位を有する金属酸化物を使った酵素的乳酸生成のための活性補酵素 1,4-NADH の電気化学的生成)

区　　分　：　甲

論　文　内　容　の　要　旨

Nicotinamide adenine dinucleotide and its hydride ($NAD^+$and NADH) are key chemicals for enhancing energy and material conversions under mild conditions in various systems. Recently, transition-metal oxides have received much attention due to their abundance, non-toxicity, good stability, and high activity in various applications. The aim of this study is the enhancement electrochemical generation of the enzymatically active coenzyme nicotinamide adenine dinucleotide (1,4-NADH) using different materials, focusing mainly on transition-metals oxides for the enzymatic electrochemical production of lactic acid.

Chapter1：General Introduction

Enzymatic electrochemical production of L-lactic acid offers several advantages over traditional chemical methods. It operates under mild reaction conditions, minimizing energy consumption and reducing the need for harsh chemicals. Electrochemistry is employed to provide the necessary driving force for the reaction and to enhance the overall efficiency of the process. The overpotential for the electrochemical generation of the cofactor NADH besides the unaffordable electrode materials are the most critical bottleneck. Therefore, providing practical and affordable solution is highly demanded.

Chapter2：Electrochemical regeneration of 1,4-NADH on Pt^{n+}- enhanced TiO_2/Ti and its application for enzymatic electrochemical production of lactic acid

TiO_2 is one of the well-known oxides in many applications specially in electrochemistry. Moreover, TiO_2 showed high selectivity and Faradaic efficiency for production of several valuable products owing to its interaction with organic molecules. The author prepared TiO_2 electrochatalyst grown on Ti electrode (TOT) and Pt enhanced TOT with different Pt content (Pt-TOT.X, X has

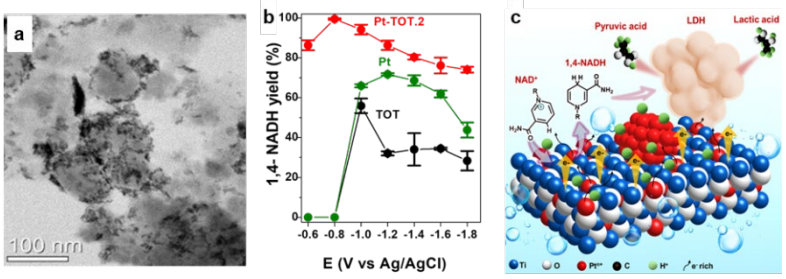

Fig.1. (a) TEM image of Pt-TOT.2 (b) yield% of 1,4-NADH generation on TOT, Pt, Pt-TOT.2, and (c) schematic mechanism of electrochemical reduction of NAD^+ for enzymatic electrochemical production of lactic acid on Pt-TOTs.

numbers from 1 up to 4 accordingly with increasing Pt content from ≈ 2 to 8 Atom.%) were prepared via one step process. TEM showed that Pt particles with high contrast form on the surface of TOT grains and a part of grain also has higher contrast (Fig. 1a). By optimizing the loading amount of Pt, the author achieved 90% generation (yield) of 1,4-NADH using Pt-TOT at the lowest potentials through the reported electrodes (–0.6V vs Ag/AgCl) and up to 100% at only –0.8V vs Ag/AgCl (as shown in Fig.1b). The remarkable performance of our best electrode Pt-TOT was brought by cooperation of predominant adsorption of NADs on TiO_2 and fast kinetics in hydrogenation realized on Pt-TOT including Pt^{n+} species taking various valence states (Fig. 1c). The electrochemically generated NADH was directly applicated to enzymatic lactic acid formation from pyruvic acid using a lactate dehydrogenase (LDH).

Chapter3 : Application of perovskite oxides for electrochemical regeneration of 1,4-NADH

The ABO_3 compounds hold a special interest due to their tunable structure and the discovery of new materials with interesting and technologically enabling target functionalities. The main objective of this study is to test perovskite oxides with stability and improved electronic transport properties for the electrochemical generation of NADH.

The prepared oxides at higher temperature gave higher yield. Among the three perovskite oxides $CaMnO_3$(CMO) achieved the highest yield over 90% for the generation of the active 1,4-NADH at –0.8 V vs Ag/AgCl (Fig. 2a), as well as the highest conversion rate of NAD^+ and selectivity for 1,4-NADH.

Chapter4 : Controlling parameters and engineering of active sites of TiO_2/Ti and Ni-TiO_2/Ti electrodes for electrochemical reduction of NAD^+

In this chapter, TiO_2 with different thickness and structure was grown on Ti mesh. Ni nanoparticles were then loaded with different amounts on the best performing TOT, and reduction treatment assisted by hydrogen spillover was subsequently used to form more active sites. The samples were designated Ni-TOT.2-1 with 10 cycles of Ni electrodeposition, Ni-TOT.2-2 with 40 cycles of Ni electrodeposition, with 10 cycles of Ni electrodeposition and hydrogen treatment (Ni-TOT.2-H), and Ni-TOT.2-2H with 40 cycles of Ni electrodeposition and hydrogen treatment. X-ray photoemission specroscopy (XPS) suggested that oxidation states of Ti species included in the prepared catalysts depend on the treatment conditions (Fig. 2.a). Ni-TOT.2-2H exhibited the highest yield of 59±2% at only –0.8 V vs Ag/AgCl and a higher yield of 93.8±1.4% at a slightly higher potential of –0.9 v vs Ag/AgCl (Fig.2. b). The catalytic activity of these electrodes is strongly modified by the presence of active sites, including Ti^{3+} and oxygen vacancies (Fig. 2.a), which act as adsorption sites for NAD^+ and then facilitate the selective hydrogenation by adsorbed H on Ni loaded particles.

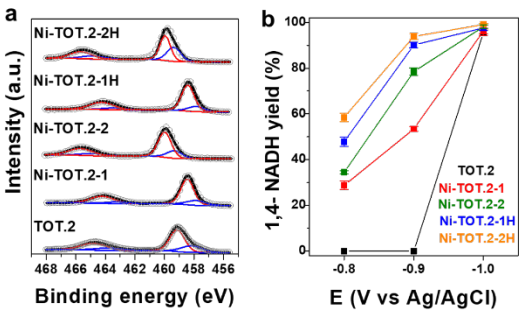

Fig. 2. (a) XPS spectra of Ti 2p, and (b) Yield% of 1,4-NADH regeneration conducted on Ni-TOT.s at low potentials.