



Robust and stable ruthenium alloy electrocatalysts for hydrogen evolution by seawater splitting



Xiaoman Niu^a, Qunwei Tang^{a,*}, Benlin He^a, Peizhi Yang^b

^a Institute of Materials Science and Engineering, Ocean University of China, Qingdao 266100, PR China

^b Key Laboratory of Advanced Technique & Preparation for Renewable Energy Materials, Ministry of Education, Yunnan Normal University, Kunming 650500, PR China

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ABSTRACT

Seawater splitting by complicated electrocatalytic processes is promising for hydrogen evolution. Here we present a series of robust electrodes by electrodeposing RuCo and RuCoMo_x alloys on Ti foil substrates for hydrogen evolution from seawater splitting. The preliminary results demonstrate that Ti foil supported RuCo and RuCoMo_x alloy electrodes require overpotentials of ~387 and ~550 mV to drive the hydrogen evolution reaction (HER) at a benchmark current density of 10 mA cm⁻², respectively. Moreover, the resultant Ti foil supported RuCoMo_x electrode shows excellent stability under persistent operation at a constant current density of -1.2 V over 12 h.

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1. Introduction

Energy crisis has been a gigantic problem for the persistent development of human society because of the dependence on fossil fuels such as coal, oil, and natural gas. Moreover, the use of fossil fuels has caused serious damages to the environment [1–4], therefore the creation of new energy with zero emissions is significantly crucial for low-carbon economy. Among various renewable resources, hydrogen energy has attracted growing interests owing to its merits on zero emission and high efficiency [5–9]. Hydrogen evolution and storage [10,11] are two main aspects for hydrogen energy utilization. Hydrogen evolution from water splitting has been a preferred technology for many years due to its advantages in producing high-purity hydrogen gas, the maturity of industrialization, no pollution [12–14], etc. However, pure water is the commonly used electrolyte, leading to the low ionic conductivity and therefore charge-transfer ability. In order to increase the ionic conductivity of target electrolyte [15], sodium hydroxide or sulfuric acid is always added into water system, resulting in great challenges in developing anticorrosion-resistant electrodes. ~75% of the earth is covered by ocean, therefore one of the most feasible routes of realizing hydrogen evolution is to catalyze seawater due to the high electrical conductivity of seawater (33.9 mS cm⁻¹ at 25 °C) and neutral condition

(pH=6.44). In this fashion, seawater splitting for hydrogen evolution is expected to avoid the complex processes by adding alkaline or acidic species, to reduce cost, and to develop diversified electrode catalysts.

The electrocatalysts for hydrogen evolution by water splitting have been widely studied, focusing on improvement of catalytic performances and reduction of the electrode cost [16]. Precious platinum (Pt) has been the most preferred electrode catalyst for water splitting because of its low hydrogen evolution potential and outstanding stability [17–20], but the high price of Pt species has been an economic burden for their commercial applications [21]. As a Pt group metal, ruthenium (Ru) is indispensable a homogeneous catalyst in a variety of organic reactions [22], but there are few studies on using Ru or Ru compounds for hydrogen evolution. Notably, the price per kg of Ru is about 10 times lower than that of Pt [22]. Ru metal has an Mg-type hexagonal close-packed (hcp) structure, making Ru fairly resistant to chemical attack during electrocatalytic processes. Moreover, Ru is unaffected by aqua regia, H₂SO₄, HCl, HF, or H₃PO₄ solutions at moderate temperatures [23].

Till now, some Ru compounds have been used as hydrogen evolution electrocatalysts, such as Ru/SiO₂ [24], RuO_x nanoparticles deposited on TiO₂ nanotube arrays [25], polypyrrole-Ru (2,2'-bipyridine)₃²⁺/MoS_x structured composite film [26], ultralow Pt loading Ru@Pt core-shell nanocatalysts [27], etc. To the best of our knowledge, there is no report on using alloyed catalysts from Ru and cost-effective transition metals as hydrogen evolution catalysts by seawater splitting. We have placed our focus on

* Corresponding author. Tel.: +86 532 66782533
E-mail address: tangqunwei@ouc.edu.cn (Q. Tang).

creating robust binary RuCo and ternary RuCoMo_x alloys on Ti foil substrates for seawater splitting. It is well known that the outermost electron orbit of Ru element is 4d⁷5s¹, while the electronegativity and lattice constant are 2.2 and 2.71 Å, respectively. Co has an outermost electron orbit of 3d⁷4s², electronegativity of 1.88, and lattice constant of 2.51 Å [28], showing that the atomic radius, electronegativity, and the lattice constants of Ru are much larger than that of Co element. Ru and Co can form *d* orbit overlap during alloying process, meanwhile, the Co atoms may enter the face-centered cubic Ru lattice to tune the binding strength between Ru and H, and to create gigantic actives for hydrogen evolution reaction (HER). According to the BREWER-ENGEL valence-bond theory [29,30], Ru and Co are the right-half of the transition elements with unpaired *d* electrons, Mo is the left-half of the transition element with a half-filled *d* orbital (4d⁵s¹), therefore the alloying of Mo with RuCo can share more *d* electrons. The extraordinary electronic structure of the ternary alloy is beneficial for providing decorated electrons for involving in HER. Electrochemical deposition is a simple technique in tuning synthesis conditions and obtaining interesting species with

high-purity, intended structures and morphologies [31]. In the current work, binary RuCo and ternary RuCoMo_x alloys are electrodeposited on Ti foils without use of any binders. The preliminary results demonstrate that Ti foil supported RuCo electrode is catalytically active toward HER, yielding an overpotential of ~387 mV vs. RHE at a current density of 10 mA cm⁻². While Ti foil supported RuCoMo_x electrode shows excellent stability at the current density about 85 mA cm⁻² over 12 h.

2. Experimental

2.1. Pretreatment of Ti foil and seawater

Before electrodeposition, the TiO_x species on Ti foil surface were removed according to the following procedures. In details, Ti foil with a thickness of 1 mm was thoroughly rinsed with deionized water, soaked in acetone under ultrasound for 30 min, and subsequently washed with deionized water to remove acetone. Finally, the freshly treated Ti foil was immersed in 1 M of oxalic acid aqueous solution and heated in a water bath at 95 °C for 2 h,

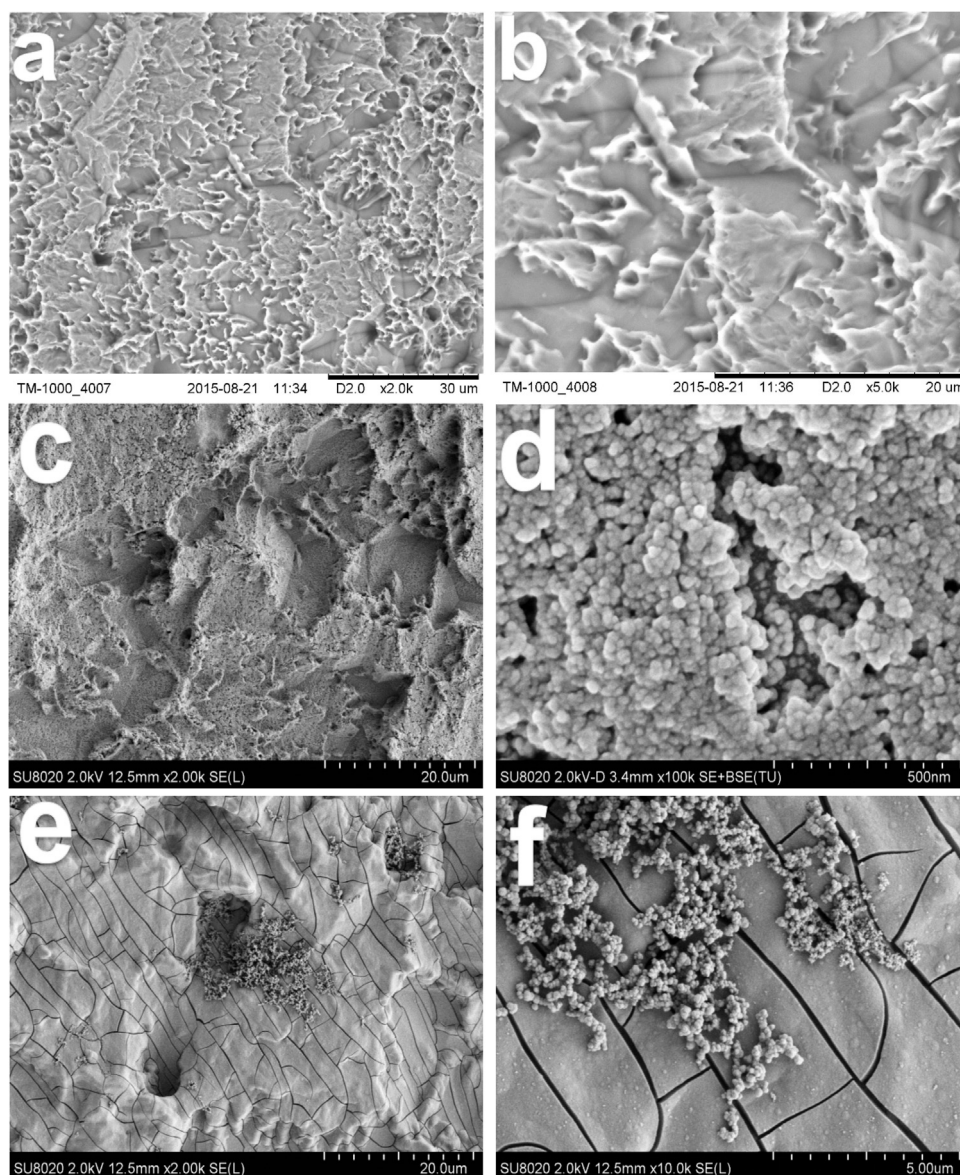


Fig. 1. Top-view SEM images of (a, b) pretreated Ti foil, (c, d) Ti foil supported RuCo alloy electrode, and (e, f) Ti foil supported RuCoMo₇ alloy electrode.

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