



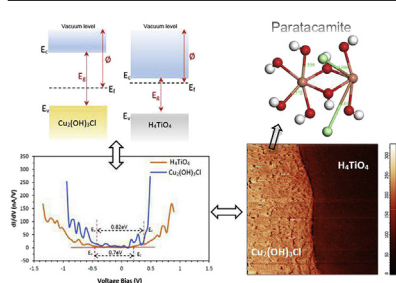
Materials science communication

TiO₂/Cu₂O coupled oxide films in Cl[−] ion containing solution: Volta potential and electronic properties characterization by scanning probe microscopyEhsan Rahimi^a, Ali Rafsanjani-Abbasi^a, Amin Imani^b, Ali Davoodi^{a,*}^a Materials and Metallurgical Engineering Department, Faculty of Engineering, Ferdowsi University of Mashhad, Azadi Square, Mashhad 91775-1111, Iran^b Materials and Polymers Engineering Department, Hakim Sabzevari University, Towhid-shahr, Sabzevar 9617976487, Iran

HIGHLIGHTS

- An accurate correlation between STS data and Volta potential of oxidized Ti/Cu couple was explained.
- TiO₂ matrix has higher Volta potential and energy band gap in comparison to Cu₂O.
- Formation of oxide compounds with new arrangement of energy levels detected after immersion test.
- TiO₂ becomes the nobler component of the galvanic couple over the time in 0.6 M NaCl electrolyte.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 10 December 2017

Received in revised form

20 February 2018

Accepted 24 March 2018

Available online 26 March 2018

Keywords:

TiO₂/Cu₂O oxides

Volta potential

Density of states

Paratacamite

Scanning probe microscopy

ABSTRACT

In this study, a combination of scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), atomic force microscopy (AFM), scanning Kelvin probe force microscopy (SKPFM), and density functional theory is applied to investigate the evolution of Volta potential and electronic properties of TiO₂/Cu₂O coupled oxides in presence of chloride-containing corrosive solution. Volta potential and the band gap of Cu₂O are increased in presence of chloride ion due to paratacamite (Cu₂(OH)₃Cl) formation whereas the opposite is seen for TiO₂ due to the formation of H₄TiO₄. The results shows a good correlation between the measured Volta potential difference and the observed corrosion behavior.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Metal oxide surfaces are one of the most widely investigated topics in physics, chemistry, and materials science due to their fundamental importance in applications such as catalysis,

microelectronics, magnetic storage media, and especially protective coatings against corrosion [1–3]. Meanwhile, many studies have focused intensively on the formation mechanisms, surface energies and electronic properties of oxide films on Ti and Cu pure metals in different media and conditions by transmission electron microscopy (TEM), atomic force microscopy (AFM), scanning tunneling microscopy (STM) and ultraviolet photoemission spectroscopy (UPS) [4–6].

TiO₂ is the most stable oxide of titanium and has an outstanding

* Corresponding author.

E-mail address: a.davodi@um.ac.ir (A. Davoodi).

resistance to corrosion and photocorrosion in atmospheric and aqueous environments in comparison with other semiconductor oxides [7]. Also, copper with high electrical and thermal conductivity slowly oxidizes in contact with an atmospheric ambient. Cuprous oxide (Cu_2O) is the most common initial corrosion product of the copper [8]. Thus, association of properties of both oxides can provide multiple necessities of good corrosion resistance and high thermal and electrical conductivity for specific applications such as aerospace, electronics, electrochemical and metallurgical equipment [9,10]. Despite numerous experimental and theoretical studies on titanium and copper oxides, there are limited data available evaluating the solid-liquid interface and electronic properties of these types of oxides as a function of time in the vicinity of each other [6]. In the case where a complete connection is available between oxides, many changes could be happened to the Volta potential, electronic property and galvanic interactivity between both oxides. Simultaneous responses of both oxides to gas or liquid media have severe effects on the adsorption mechanism and reactivity of the adsorbates on their surfaces [4,7,11–13].

In this study, multi-technical analysis including atomic force microscopy (AFM), scanning Kelvin probe force microscopy (SKPFM), scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) was performed in order to have a deeper understanding of electrochemical nobility and the density of states on $\text{TiO}_2/\text{Cu}_2\text{O}$ surface. The distribution of the Volta potential along with the normalized differential conductance (dI/dV) extracted from the I-V curves of STS which are proportional to the surface density of electronic states [14–16].

2. Experimental

To produce a $\text{TiO}_2/\text{Cu}_2\text{O}$ coupled sample, an industrial explosively welded pure Ti-Cu bimetal sheet was used. The flyer plate in the explosively joint sample is Ti sheet with a thickness of 3 mm and the base plate is a copper sheet with a thickness of 27 mm. The sample was received as a large plate with a size of $200 \times 200 \times 30$ mm. A massive specimen of Ti-Cu bimetal was cut into a cube for STM/STS and AFM/SKPFM analysis with a surface area of 1.25 cm^2 . The specimen was ground with SiC paper up to 3000 grit, polished and ultrasonically cleaned in ethanol. Two automatically interchangeable measuring heads (SKPFM and STM), which are integrated into the Solver Next AFM instrument, were used. An n-doped silicon pyramidally-shaped tip was used for all SKPFM measurements. SKPFM measurements were performed in amplitude modulation (tapping mode) at ambient temperature with relative humidity of 25%, pixel resolution of 512×512 and scan frequency rate of 0.3 Hz. For STM/STS measurements, Pt-Ir tip was sharpened by cut-and-pull technique at about 60° angle with a special cutting scissor. The tip-sample distance was fixed by applying a constant bias voltage of 1 V and a set point current of 0.4 nA. In order to investigate the normalized differential conductance spectra, the tunneling currents were recorded in the scanning voltage range of -1.5 V to $+1.5 \text{ V}$ with a scanning rate of 400 mV/s . In order to perform the quantum chemical calculations of paracetamol, DMol3 modulus based on density function theory (DFT) in “Materials Studio 5.0” software was employed for investigation of Quantum chemical parameters such as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

Galvanic measurement of $\text{TiO}_2/\text{Cu}_2\text{O}$ couple was carried out in two separate electrodes with same area (1 cm^2) in 0.6M NaCl solution for investigation of the polarity reversal time. Galvanic experiments and potentiodynamic polarization measurement were performed with a Gill AC potentiostat (ACM) along with a saturated calomel electrode (SCE) and a platinum foil used as the reference

and counter electrode, respectively.

3. Results and discussion

3.1. SKPFM and STS investigations

A schematic illustration for the energy-level diagram of TiO_2 and Cu_2O oxides is illustrated in Fig. 1a using analysis of SKPFM mapping (Fig. 1b) and STS data (Fig. 1f) of STM images (Fig. 1d and e). SKPFM image showed that the highest value of Volta potential is related to TiO_2 matrix with the mean value of 400 mV while the lowest value corresponds to Cu_2O matrix with the mean value of 52 mV. This large Volta potential value difference (Fig. 1c) or driving force ($\Delta V = 348 \text{ mV}$) indicates the difference in work function values which is equivalent to their difference in Fermi level position in non-contact state [17,18]. In fact, Cu_2O has the Fermi level (E_F) close to the conduction band (E_C) while the Fermi level of TiO_2 is near to valence band (E_V), as shown in Fig. 1f which is similar to UPS band edges results of Greiner et al. [3].

The minimum density of states is assigned to the surface electronic gap (E_g) of the oxide films. TiO_2 and Cu_2O show band gap values of 2.1 eV and 0.5 eV along with steeply rising lines in Fig. 1f which are lower than expected values for the bulk oxide films (3.2 eV and 2.17 eV, respectively) due to the presence of different surface states (or surface defects) [3,19,20]. Total tunneling current depends on the number of surface electronic states because the presence of numerous surface states (peaks) regarding surface defects and other adsorbates from the air (surface adsorbed OH^-) increases the specific surface area of the oxide films which leads to act as the new electronic states for electron tunneling [15,21].

Oxide films with more n-type conductivity exhibit larger tunneling current at negative sample bias voltages in I-V or dI/dV -V curves in comparison to positive sample bias voltages. The ratio between tunneling charge of occupied states and unoccupied states of the oxide surface can be used as n-type or p-type semiconductor character [22]. According to Fig. 1f, TiO_2 and Cu_2O show high charge ratio along with higher tunneling current at negative bias voltages which means that both oxides have more n-type semiconductor character. The work functions of most noble materials are usually higher than those with lower nobility [14,17]. As a result, TiO_2 behaves as the noble site during immersion in the electrolyte, while Cu_2O behaves like the active region which finally leads to the net flow of electrons from Cu_2O to TiO_2 , as shown in Fig. 1c. In fact, the Volta potential distribution on metal oxide surface has usually been detected in air using SKPFM technique and its value depends on the work function of the metal oxide, surface condition and environmental conditions [21,23]. So, high value of work function and Volta potential indicate a high electrochemical nobility and it can be considered as a criterion for prediction of corrosion behavior [23].

The surface electronic properties of Cu_2O and TiO_2 are important because the surface conductivity is the important quantity for electrochemical activity. An increase in work function of TiO_2 reflects a higher stability of valence electrons leading enhanced resistance to corrosion attack in comparison with Cu_2O because a more stable electron state in TiO_2 limits valence electrons to participate in electrochemical reactions [24]. Also, the low value of Volta potential or work function on Cu_2O in comparison with TiO_2 can be explained as an increasing tendency for electron transfer. Therefore, Cu_2O in the electrolyte media could be susceptible for more corrosion attacks and anodic electrochemical reactions.

During immersion of the $\text{TiO}_2/\text{Cu}_2\text{O}$ coupled sample in 0.6M NaCl solution for 3600 s, a noticeable evolution observed in the microstructure, Volta potential and electronic properties of both. SKPFM analysis showed that the Volta potential distribution on $\text{TiO}_2/\text{Cu}_2\text{O}$ changed along with the formation of new oxide films.

Download English Version:

<https://daneshyari.com/en/article/7921631>

Download Persian Version:

<https://daneshyari.com/article/7921631>

[Daneshyari.com](https://daneshyari.com)