

POSTECH 2017 환경연수프로그램

Electro Catalysts Development for Application in Wastewater Treatment (하·폐수처리용 촉매 소재/전극 개발)

이름 : 김지선(Kim Ji Seon)

소속 : 영남대학교 화학공학부(Yeungnam University)

지도교수님 : 조강우 교수님

참여 연구실 : 하폐수 변환 가속화 연구실

1. Introduction

The effective treatment of effluents represents a serious problem, especially for the chemical industry. Over the last twenty-five years, huge efforts have been made to limit at the source this type of pollution, by improving processes, recycling products and controlling the treatment of wastes at the production stage. However, considering the large amounts of industrial effluents to be treated, for example to retrieve certain solvents, there are inevitably residues requiring a final transformation, which is often delicate. Traditional destruction methods, for their part, pose problems of corrosion and, more seriously, of emissions, if the treatment conditions are not perfectly controlled.

From the industry point of view, this problem must be examined as a whole since there are no universal or simple methods in this area. The wide variety of industrial discharges means that a diversification of techniques must be sought, adapting the treatment to each situation, as much as possible. In spite of the efforts made to develop clean processes, the increasingly severe environmental

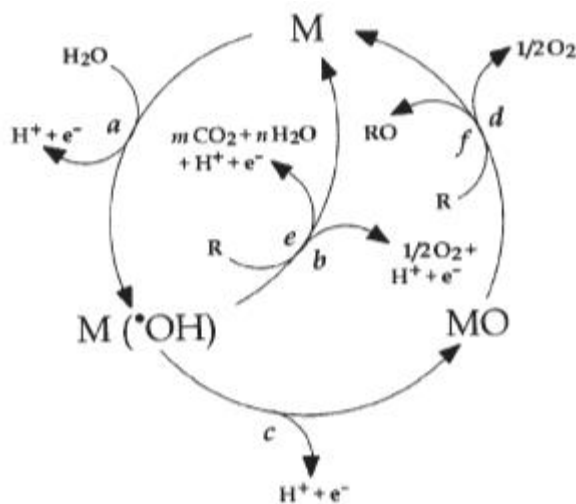
laws should encourage the research for better-performing treatments, making it possible to obtain environmentally compatible effluents.²⁶ Actually, the processes for the treatment of wastewater may be divided into three main categories: primary, secondary and tertiary. Tertiary treatment, also known as advanced wastewater treatment, includes acid/base neutralization, precipitation, reduction and oxidation processes.

Electrochemical technologies for wastewater treatment

Electrochemical technologies have gained importance in the world during the past two decades. There are different companies supplying facilities for metal recoveries, the treatment of drinking water as well as process waters resulting from tannery, electroplating, dairy, textile processing, oil and oil-in-water emulsion, etc. At present, electrochemical technologies have reached such a state that they are not only comparable with other technologies in terms of cost, but sometimes they are more efficient and compact. The development, design and application of electrochemical technologies in water and wastewater treatment has been focused on particularly in some technologies such as electrodeposition, electrocoagulation, electroflocculation and electrooxidation.

Direct and indirect electrochemical oxidation

Electrochemical oxidation mechanism



Electrochemical oxidation of pollutants can occur directly at anodes through the generation of physically adsorbed “active oxygen” (adsorbed hydroxyl radicals) or chemisorbed “active oxygen” (oxygen in the oxide lattice, $\text{MO}_x + \text{I}$). This process is usually called “anodic oxidation” or “direct oxidation” and the course for the anodic oxidation was described by Comninellis: the complete destruction of the organic substrate or its selective conversion into oxidation products is

schematically represented in Fig. When a toxic, non-biocompatible pollutant is treated, the electrochemical conversion transforms the organic substrate into a variety of metabolites; often, biocompatible organics are generated, and biological treatment is still required after the electrochemical oxidation. In contrast, electrochemical degradation yields water and CO_2 , no further purification being necessary. Nevertheless, the feasibility of this process depends on three parameters: (1) the generation of chemically or physically adsorbed hydroxyl radicals, (2) the nature of the anodic material and (3) the process competition with the oxygen evolution reaction.

A mechanism for the electrochemical oxidation of organics, based on intermediates of oxygen evolution reaction in aqueous media, was formerly proposed by Johnson. The process involves anodic oxygen transfer from H_2O to organics via hydroxyl radicals formed by water electrolysis.

The electrochemical oxidation of some organics in aqueous media may take place without any loss in electrode activity, except at high potentials, and with concomitant evolution of oxygen. Furthermore, it has been described that the nature of the electrode material strongly influences both the selectivity and the efficiency of the process. To interpret these observations, a comprehensive model for the anodic oxidation of organics in acidic medium, including the competition with the oxygen evolution reaction, has been proposed. More recent results, obtained at conductive diamond electrodes (which are characterized by a very high oxygen overpotential), fit the model predictions quite well. Based on these results, Comninellis explained the differences considering two limiting cases, i.e. the so-called “active” and “non-active” anodes.

Recent advances in wastewater treatment include electrochemical systems where reactive chlorine is often the primary oxidant for pollutant abatement. Successful implementation of the electrochemical water treatment systems depend on the efficacy of a chlorine evolving anode operating in dilute aqueous solutions. We developed new heterojunction mixed metal oxides anodes, which allow for enhanced reactive chlorine generation in dilute aqueous solution in terms of current (energy) efficiency, for primary usage in advanced wastewater treatment. The outer surface of the heterojunction anodes is functionalized with $\text{Bi}_x\text{Ti}_{1-x}\text{O}_2$ layers which provide elevated electro-stationary concentration of adsorbed hydroxyl radical, while the underlying $\text{Ir}_{0.7}\text{Ta}_{0.3}\text{O}_2$ layer serves both as Ohmic contact and electron shuttle. This study demonstrates that the surficial binary metal oxides layers, prepared through traditional thermal decomposition of aqueous Ti and Bi complex solutions, not only shift the heterogeneous kinetics and selectivity but also reduce the loss of iridium under long term operation.

2. Experiment

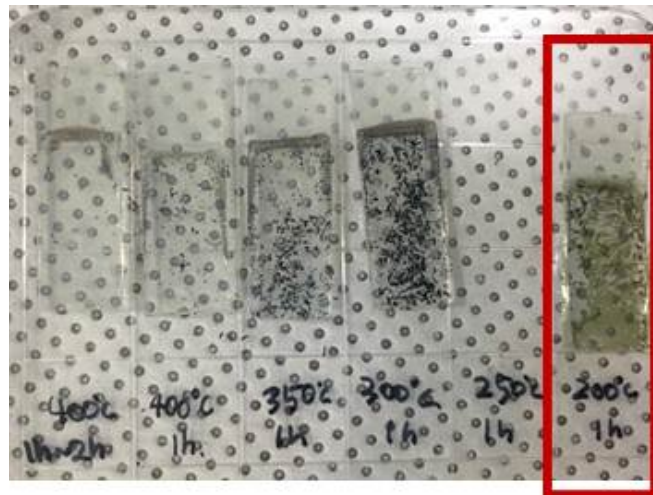
- Nickel(II) nitrate hexahydrate, 99% for analysis \rightarrow 0.1M
- 1×3 FTO glass (reaction region, 1×2)
- Chronopotentiometry
- Cathodic current : $-10\text{mA}/\text{cm}_2$ $\therefore -20\text{mA}$
- Electrodeposition time : 5min



Working electrode
Counter electrode

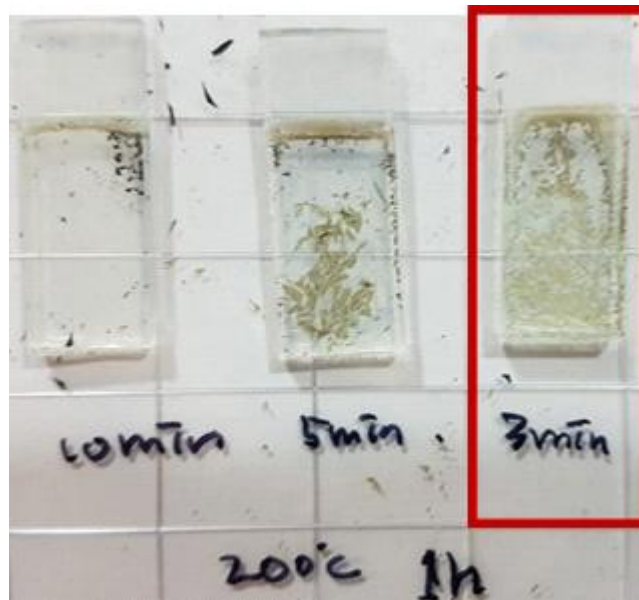


-위의 조건은 다 같게 한 후, Annealing 온도를 조절하여 실험을 함.



\rightarrow Annealing 하는 온도가 300°C 이상일 때, $\text{Ni}(\text{OH})$, NiOOH 가 ash로 되는 것을 볼 수 있었다.

- Annealing 온도를 $200^\circ\text{C}(1\text{hr})$ 을 기준으로 삼고, 일단 변수로 electrodeposition time을 조절해봄.



→ Electro deposition time이 3min일 때가 표면에서 붙어있는 것을 볼 수 있었다. 그에 비해, electro deposition time이 길었던 것은 표면에 붙어있지 못하고 떨어지는 것을 관찰 할 수 있었다.

∴ 이렇게 electro deposition time을 3min으로 적정한 후 다른 변수들을 조절해보았다.

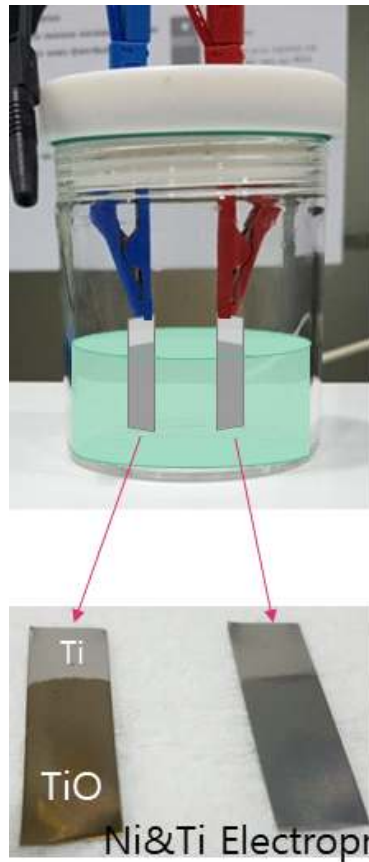
- Electro deposition time : 3min, annealing 시간을 조절해봄.



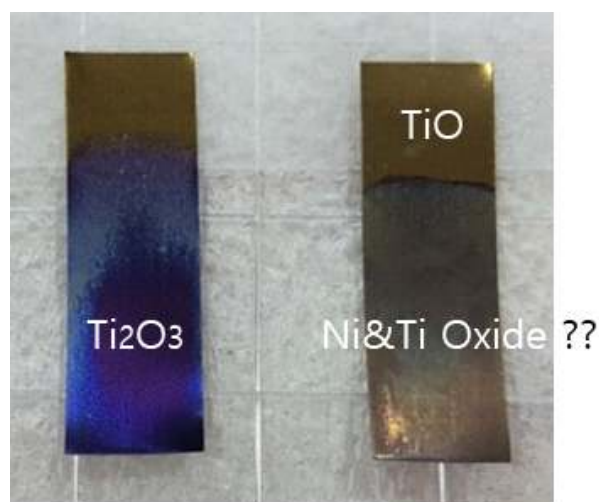
즉, 200°C에서 (3min, 5min, 10min)으로 annealing시켜보고, 300°C에서 (3min, 5min)으로, 400°C에서 (1min, 3min)으로 annealing을 해보았습니다. 후에 관찰 해본 결과, crystallization이 일어나지 않은 것 같고, 또는 ash로 변화한 모습 이였습니다.

이렇게 결과가 나오는 이유로는 FTO glass는 이미 crystallized가 이루어져있기 때문에, 또 다른 MO_x layer가 그 위에 쌓여지는 것이 어려운 것으로 보였습니다. 따라서 다음 실험에서는 FTO glass를 Titanium foil로 대체해서 실험해보기로 결정하였습니다.

- Substrate : Titanium foil
- Working electorode → cathodic current : -5mA, -1mA, -50uA (continuously) → 3minute



- Working electrode와 Counter electrode 모두 Titanium foil을 사용하여 electro deposition 한 후에 각각을 모읍입니다. (즉, annealing 하긴전)
- Annealing : 400°C (1hr)



- Annealing을 한 뒤의 working electrode와 Counter electrode모습입니다. Counter

electrode 경우에는 electro deposition 시켰을 때는 금빛이 도는 모습이 보였는데, annealing을 시키고 난 뒤에는 푸른빛을 보는 것을 관찰 할 수 있었습니다. 그래서 Titanium이 산화 되면 어떠한 색이 되는 지 알아보기 위해 찾아 본 결과 titanium이 산화가 될 수로 밑에 참고한 사진과 같이 색깔이 변화는 것을 알 수 있었고, annealing 하기 전에는 TiO , annealing 한 후에는 Ti_2O_3 일 것이라고 예상해 볼 수 있었습니다.



- 이때까지 FTO 위에 electro deposition을 이용하여 만든 전극을 test 해보기 위해 Linear Sweep Voltammetry(1M KOH)를 찍어보았습니다.

● LSV 찍기 전●

Electrodeposition time : 3min

NiOx 200도 3min

NiOx 200도 5min

NiOx 200도 10min

NiOx 300도 3min



No annealing
 Ni(OH)_2



1M KOH

●LSV 찍은 후●

Electrodeposition time : 3min

NiOx 200도 3min

NiOx 200도 5min

NiOx 200도 10min

NiOx 300도 3min



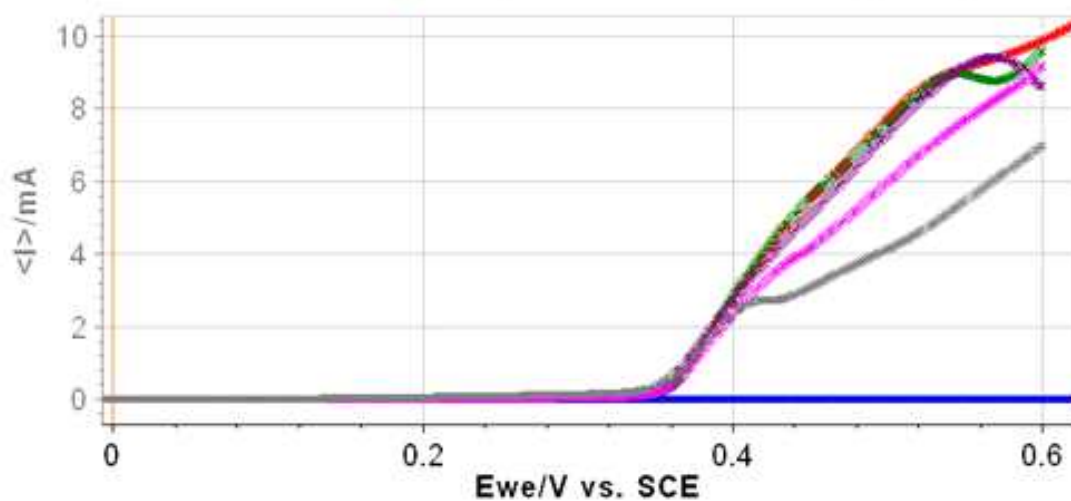
→ No annealing
Ni(OH)₂



1M KOH

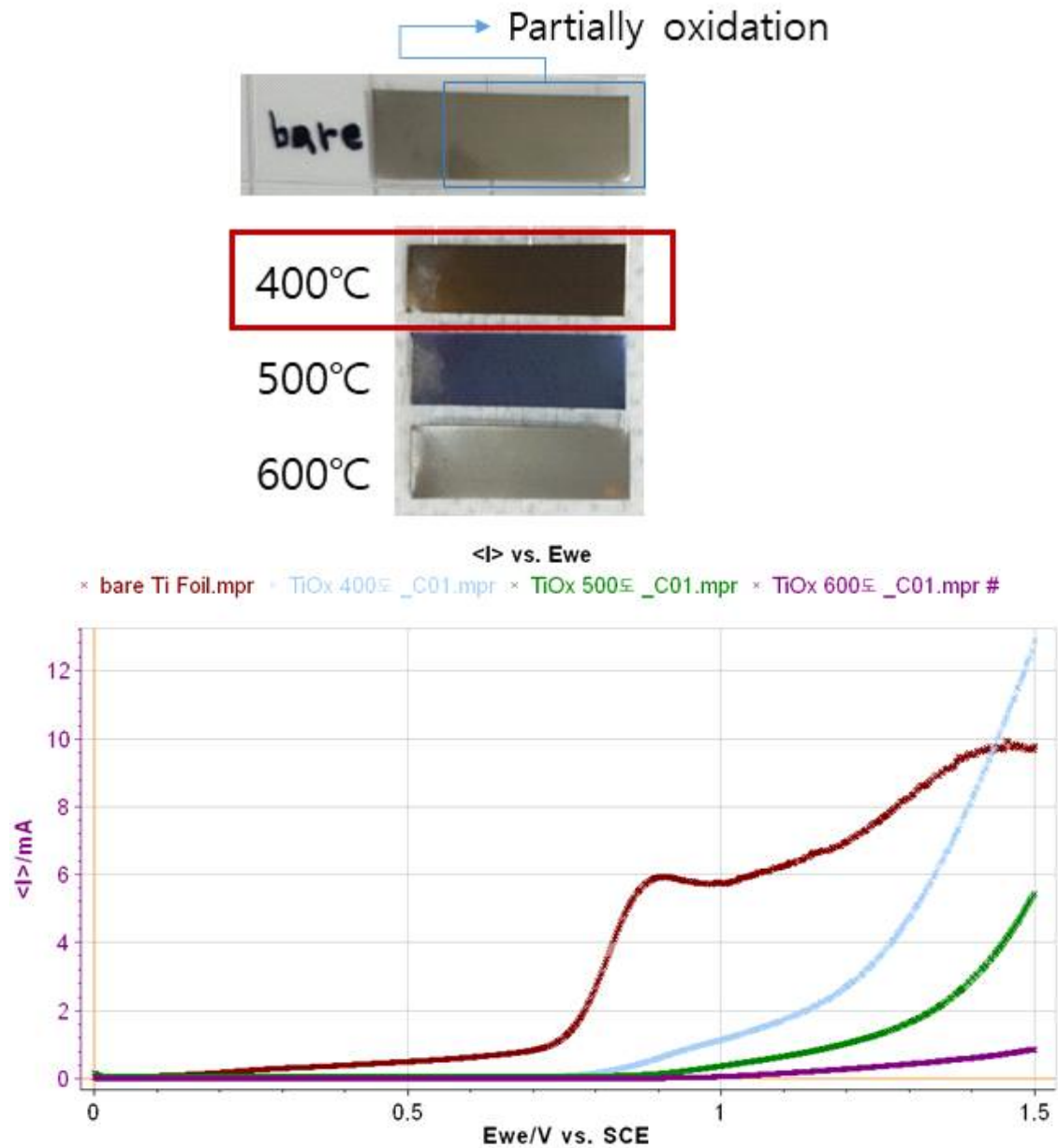
<I> vs. Ewe

- × bare FTO_C01.mpr
- × Ni(OH)₂ FTO_C01.mpr
- × NiOx 200도 3min FTO_C01.mpr
- × NiOx 200도 10min FTO_C01.mpr
- × NiOx 200도 5min FTO_C01.mpr
- × NiOx 300도 3min FTO_C01.mpr #



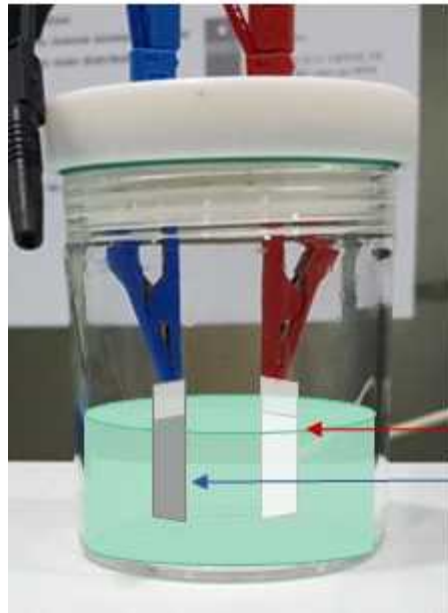
∴ Ni(OH)₂ & NiOx on FTO glass worked in LSV, but are combusted.

-Annealing Temperature Optimization을 하기 위해 Titanium foil을 400°C, 500°C, 600°C로 annealing 시킨 후 LSV를 찍어보았습니다.



∴ 400°C 가 가장 적절한 것을 볼 수 있었습니다.

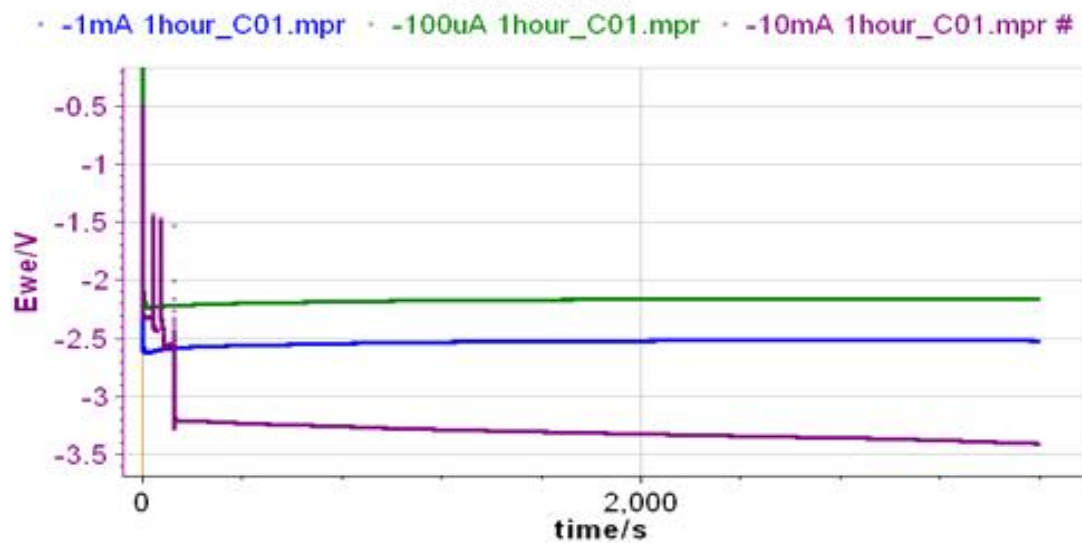
- 따라서 Ti을 electro deposition할 때 어느 정도의 전류가 가장 최적인지 알아보기 위해 가하는 전류를 달리 하여 실험 해보았습니다.



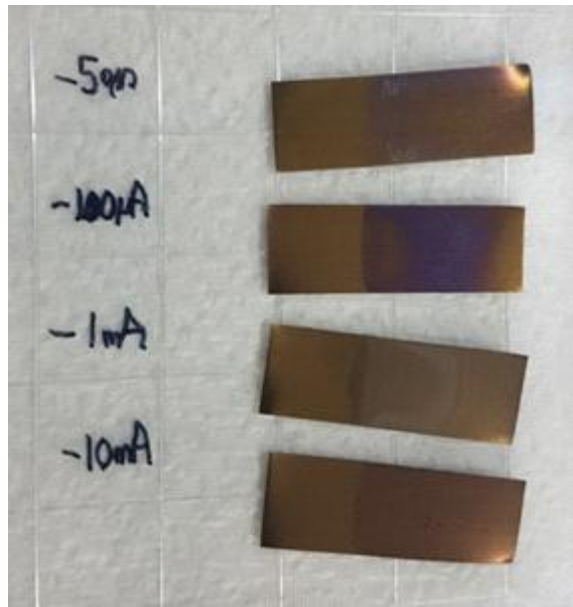
-50 μ A, 1hour
 -100 μ A, 1hour
 -1mA, 1hour
 -10mA, 1hour

FTO
 Ti Foil

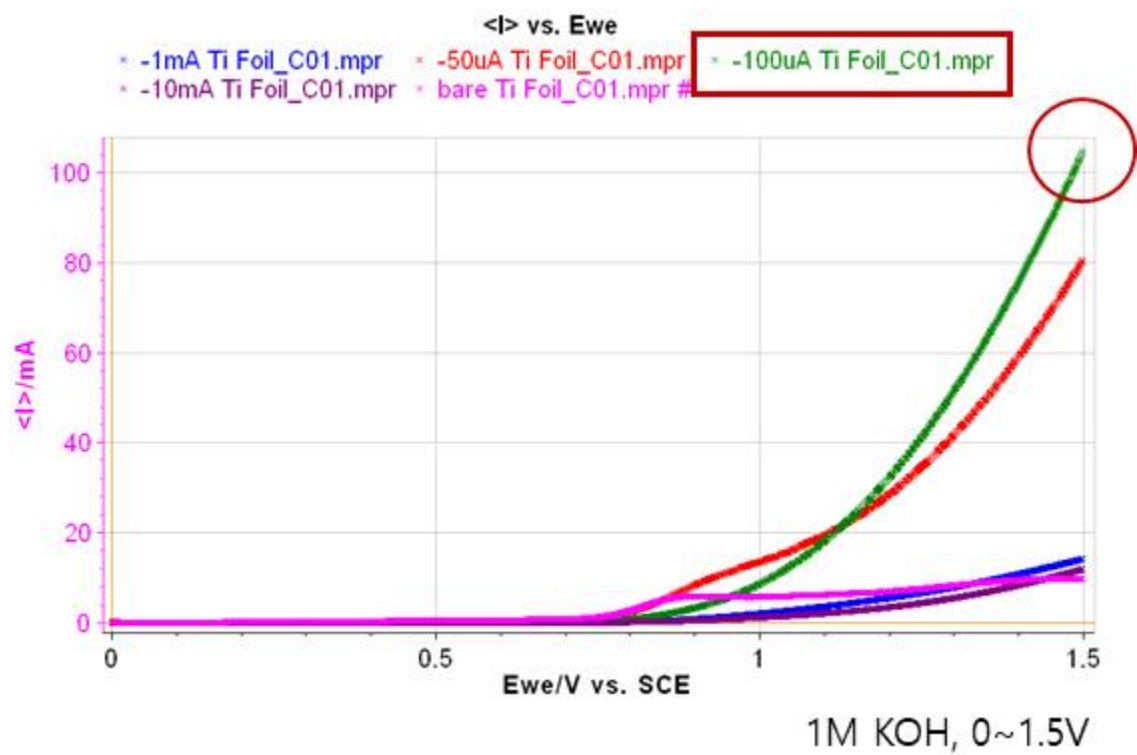
Ewe vs. time



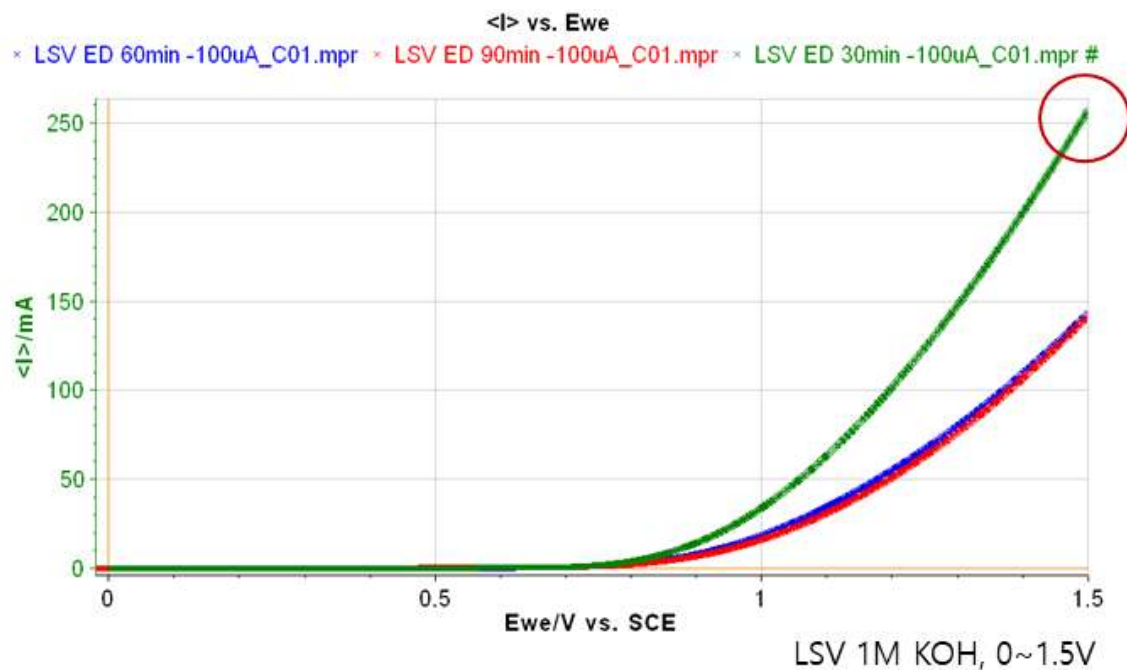
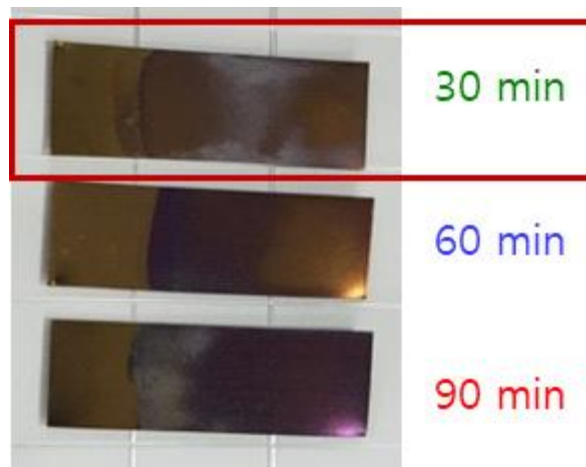
- electro deposition을 거치고 난 후에 annealing 온도는 400°C로 최적화하였기 때문에, 이 온도로 annealing을 시켜줍니다.



-이를 LSV(Linear Sweep Voltammety) 방법을 이용해서 찍어보았습니다.



- 그리고 electrodeposition time optimization(-100uA, Cathodic current)



∴ 이를 통해 electrodeposition을 30min 근처에서 더 최적화를 해박야한다는 것을 알 수 있었습니다.

3. Conclusion

금속을 electrodeposition 방법을 이용하여 전극위에 deposition 시켜서 전극을 만들어서 좀 더 빠르고 효율이 좋고, 또한 전극 수명을 좋게 하기 위해, 어떤 종류의 금속을 이용할 것인지에 따라서도 달라지는 것을 알 수 있다. 또한 한 가지의 종류만을 쓰는 것이 아니라 그 이상의 금속을 이용하여 얼마나의 배율로 사용하는 지에 따라서도 효율이 달라진다. 따라서 이번에는 Nickel(II) nitrate hexahydrate을 이용하여 deposition을 시켜보았다. 아직 최적화가 덜 되었지만 electrodeposition의 시간, annealing 온도, annealing 시간을 조절 해 봄으로써 LSV가 변화하는 양상을 볼 수 있었다.

4. Reference

[1] Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes

Carlos A. Martínez-Huitle* and Sergio Ferro

Received 21st April 2006 First published as an Advance Article on the web 10th July 2006 DOI: 10.1039/b517632h

[2] BixTi1-xOz Functionalized Heterojunction Anode with an Enhanced Reactive Chlorine Generation Efficiency in Dilute Aqueous Solutions Kangwoo Cho^{†,‡} and Michael R. Hoffmann*,[†]

[3] Direct And Mediated Anodic Oxidation of Organic Pollutants

Marco Panizza* and Giacomo Cerisola

Department of Chemical and Process Engineering, University of Genoa, P.le J. F. Kennedy 1, 16129 Genoa, Italy

Received April 2, 2009