Durability and Activity of Modified Nickel Anode for Alkaline Water Electrolysis

H. Ichikawa, K. Matsuzawa, Y. Kohno, I. Nagashima*, Y. Sunada**, Y. Nishiki***, A. Manabe***, and S. Mitsushima

Yokohama National University, *Kawasaki Heavy Industries, Ltd., **Chlorine Engineers Corp., Ltd., ***Permelec Electrode Ltd.

79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
*1-1 Kawasaki-cho, Akashi 673-8666, Japan
**7F Sakura Nihonbashi Buildings, 1-13-12 Nihonba-shi Kayaba-cho, Chuo-ku, Tokyo 103-0025, Japan
***2023-15 Endo Fujisawa 252-0816, Japan

Introduction

Alkaline water electrolysis (AWE) produces highly pure hydrogen with simple and less expensive configuration. Therefore, it will be very important process for "Green hydrogen" which is produced from water using renewable energies[1]. The renewable energies such as wind turbine and solar cells supplies unstable electric power to AWE; therefore, AWE is required durability under potential cycling.

Conventional anode is Ni based material in AWE[2]. It is stable in steady electrolysis, but it corrodes easily with potential cycling which simulates fluctuation of the renewable energies[4].

In this study, the durability and catalytic activity of modified Ni anode for oxygen evolution reaction (OER) has been investigated under potential cycling and discussed the effect of pre-oxidation as a basic study for the combination of AWEs and renewably energies.

Experimental

Working electrodes were modified Ni electrodes called Ni, NiO or (Li)NiO. The NiO was a sintered Ni plate (The Nilaco corp., 99.+%) at 800°C in air. The (Li)NiO was a sintered Ni plate (The Nilaco corp., 99.+%) with 1.49 mgcm^{-2} of LiOH at 800°C in air. A counter and a reference electrode were a Ni coil and a reversible hydrogen electrode (RHE), respectively. All measurements were performed with a three-electrode electrochemical cell at 25°C. The electrolytes were in 7.0M (=moldm^{-3}) of KOH.

Cyclic voltammetry (CV) was applied for 100 cycles between 0 and 1.5 V vs. RHE with the scan rate of 100mVs^{-1} as an electrochemical pretreatment. After that, the CV between 1.0 and 1.8 V vs. RHE with the scan rate of 1Vs^{-1} was applied for the duration protocol. The catalytic activity of the OER was evaluated by slow scan voltammogram (SSV) between 0.7 and 1.8 V vs. RHE with the scan rate of 5 mVs^{-1} before and after the deterioration protocol. The resistance of oxide film by sinter (R_f) was evaluated by AC impedance technique at bias potential from 1.6 V vs. RHE to 1.8 V vs. RHE before and after the duration protocol.

Results and discussion

Figure 1 shows the SSVs of the Ni, NiO and (Li)NiO electrode during deterioration protocol in 7.0M KOH. Onset potential of the OER of the NiOs were smaller than that of the others. But the OER current of the NiOs were smaller than that of the others above ca. 1.5 V vs. RHE because of linear relation between the OER current and the potential. Redox peaks around 1.3 V vs. RHE corresponds to the following reaction[3].

$$Ni(OH)_2 = NiOOH + H^+ + e^-$$

These peaks of the (Li)NiOs was larger than that of the NiOs, and grew up with potential cycling. On the other hand, these peaks of the NiOs almost unchanged after potential cycling. The oxide film of the NiOs would be denser than that of the Ni and (Li)NiOs, and thinner layer of the NiOs would contribute to the redox reaction compared with the Ni and (Li)NiOs. Therefore, the resistance of the inner oxide film of the NiOs affected to the linear relation between the OER current and the potential. The (Li)NiOs would be more porous, and have larger surface area than the NiOs.

Figure 2 shows the dependence of the potential at 10 mAcm^{-2} of the OER ($E_{@10mA}$), the charge (Q_c) of the redox peak in cathodic sweep and the R_f as a function of the potential cycle number in 7.0M KOH at 25°C. Here the R_f is only for the (Li)NiO. The $E_{@10mA}$ corresponds to the anode overpotential of the OER. At the initial period, the $E_{@10mA}$ of Ni was smaller than that of the others. The $E_{@10mA}$ of the Ni increased with potential cycling, but that of the NiO and the (Li)NiO decreased with potential cycling with linear function. The $E_{@10mA}$ of the (Li)NiO was smaller than that of the Ni after 15000 cycles. The R_f of (Li)NiO decreased with potential cycling. Therefore, the thickness of the surface porous oxide layer for the NiO and the (Li)NiO would increase, and the thickness of the inner dens layer would decrease with potential cycling, and this behavior affected the decrease of overpotential with potential cycling.

From these results, control of the oxide structure improves the catalytic activity and durability of the anode for the AWE.

Reference

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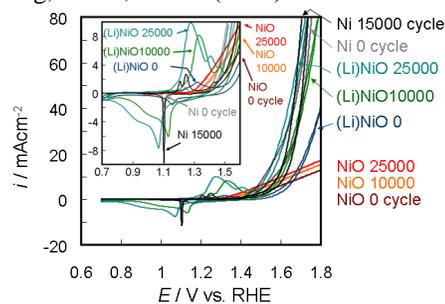
Fig. 1 SSVs of NiO and LiNiO electrode during degradation protcol in 7.0M KOH solution.
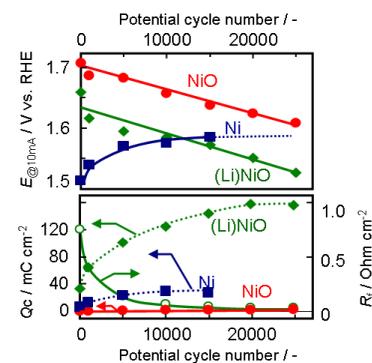
Fig. 2 Dependence of the $E_{@10mA}$, Q_c and R_f of Ni, NiO and (Li)NiO electrode during degradation protocol for potential cycle number in 7.0M KOH solution at 25°C..