XPS characterization of electrodes for alkaline water electrolysis

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Introduction

Hydrogen is important for the chemical industry but also for an enviromental friendly energy economy in which hydrogen is needed for energy storage.
Water electrolysis is - besides reformation of natural gas - the dominant production method for hydrogen. The alkaline electrolysis is typically used for technical plants because non-noble metals can be used as catalysts. Nickel is a standard catalyst for the alkaline electrolysis.

Preparation of electrodes at DLR

At DLR electrodes for high efficient alkaline electrolysis are prepared in two steps. The first step is the coating of a nickel sheet with the catalytic layer and in a second step the electrode is activated. Raney-nickel prepared from a nickel aluminum alloy is used as basic material. The basic powder is oxidized. By adding molybdenum to this alloy, the catalytic activity of the cathodes can be further improved. To improve the anode catalyst cobalt oxid is added. The electrodes are prepared by vacuum plasma spraying (VPS). With the VPS a nickel perforated-metal-sheet as substrat is coated with the catalyst layer (Fig. 1).

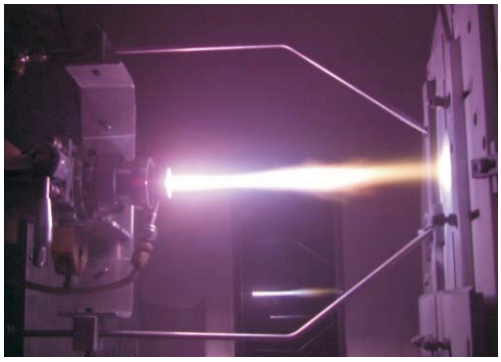

Fig. 1: Low pressure plasma spraying

The coated layer which is completely oxidizied has a thickness of few 10 µm. Atherefore, a second step in order to activate the electrodes is necessary. For this purpose the aluminina in the electrodes is dissoved in KOH (Fig. 2). By dissolution of the Al a highly porous catalyst layer is formed. Due to the activation process hydrogen is generated by the dissolution of the Al. Therefore, hydrogen partially reduce the nickel oxide and a pyrophobic layer will be formed, consequently, the air contact with an dry electrode must be avoid.

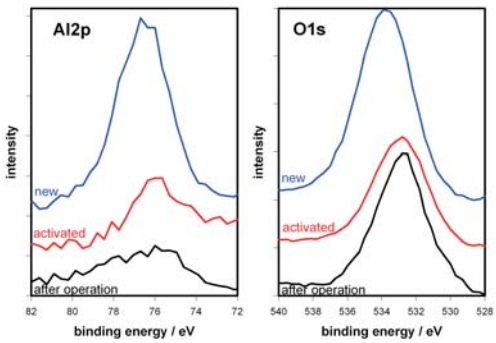

Fig. 2: Al 2p spectra (left side) and O 1s spectra (right side) measured on a non-activated, an activated and an operated cathode

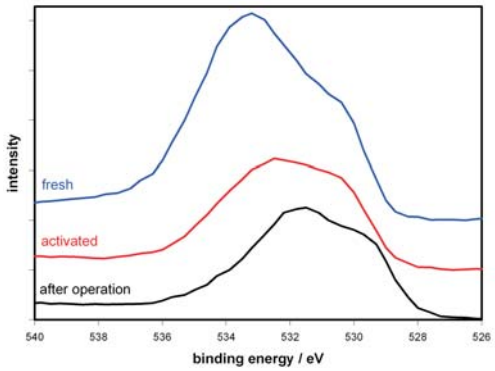

Fig. 3: O 1s spectra of the non-activated, activated and operated anode

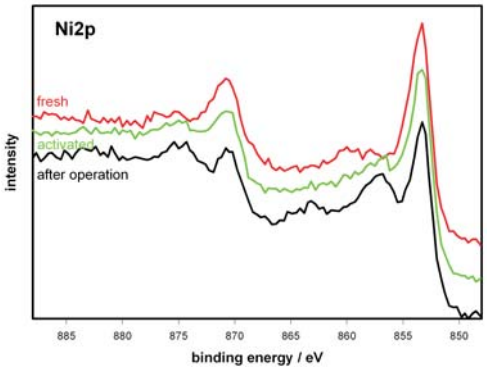

Fig. 4: Ni 2p spectra of the non-activated, activated and operated cathode

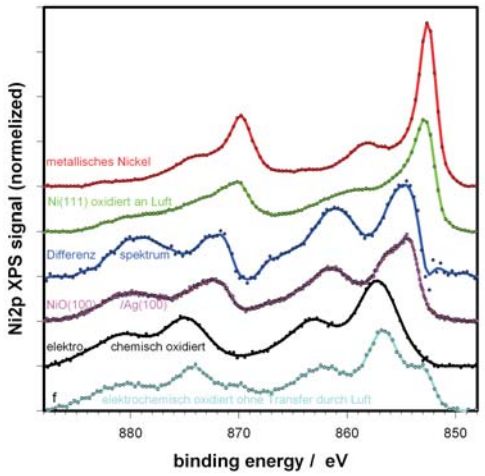

Fig. 5: Ni 2p spectra of nickel in different oxidation states, prepared under well defined conditions

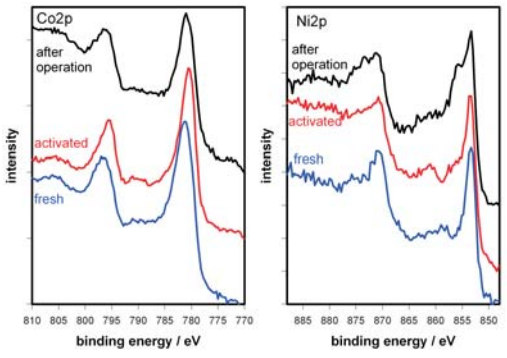

Fig. 6: Co 2p (left) and Ni 2p spectra (right) of the non-activated, the activated and the anode

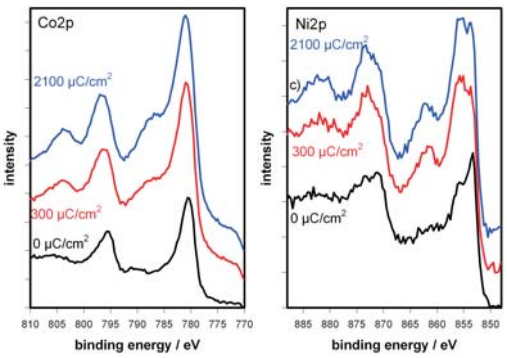

Fig. 7: Co 2p (left) and Ni 2p spectra (right) of an activated anode after different periods of etching

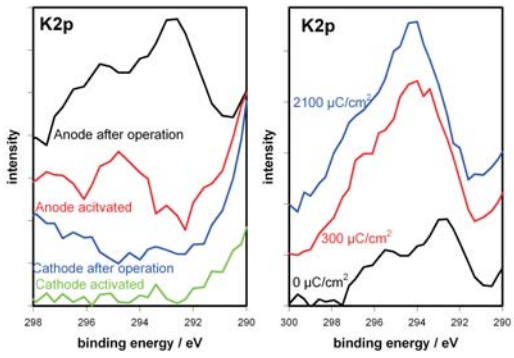

Fig. 8: K 2p spectra of a an activated and an operated anodebefore and after ion etching (left) and K 2p spectra of the operated anode after different periods of ion etching

Results

The electrodes were investigated after preparation by LPPS, after activation and after operation.
Fig. 2 shows that the alumina is mainly dissolved during the activation procedure, during operation some of the residual Al is also dissolved. Also the O 1s spectrum changes during operation. The peak shift of the O 1s signal indicates the alteration of the oxide form from metal oxide to metal hydroxide for the used cathodes.
The same alteration in the oxide state can also observed for the used anodes (Fig. 3)
Nickel as main catalytic component changes the oxidation state (Fig. 4). The different oxidation states of nickel can be distinguished as shown in Fig. 5. In the spectra a change of the oxidation state of the nickel can be observed. After operation the nickel is in an oxidized state.

The alterations in the Co 2p spectra of the non-activated, the activated and the operated anode differ not significantly (Fig. 6). The activated anodes was investigated after different periods of ion etching. In the Fig. 7. with the etching depth more cobalt oxide occurs as well as also more nickel oxide.
In addition, the potassium signal of the activated electrode (in KOH) and after operation. on the surface of the operated anode potassium could be detected. The ion etching experiments indicated the the potassium is intercalated in the electrode.

Conclusions

- Raney-nickel dopped with molybdenum for cathodes and dopped with Co_3O_4 for anode electrolyzer electrodes can be prepared by VPS
- Alumina in the Raney-nickel is dissoved mainly during the activation process
- Residual Al is dissoved during operation
- The oxidation state of the metals is changed after operation
- On the surfaces of the activated electrodes and of the used electrodes the trivalent nickel oxide could be observed
- The stability of the cobalt in the anodes is high, no significant alteration in the cobalt signal is observed
- Potassium is intercalated in the operated anodes (in the oxide film)