DEVELOPMENT OF HIGH PERFORMANCE CATHODES FOR HYDROGEN PRODUCTION FROM ALKALINE SOLUTIONS

H. Kronberger,* Ch. Fabjan and G. Frithum
Technical University of Vienna, Getreidemarkt 9, A-1060 Wien, Austria

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Abstract—Ni-based mixed catalysis were tested as hydrogen generating cathodes in alkaline solutions. Low activation energies and low overvoltage was found on binary Ni/TiH catalysts indicating high catalytic activity. The best results under technical operating conditions were obtained on activated plasma-sprayed Raney-alloy coatings and sintered ternary Ni/B/TiH, and are rather a consequence of optimized surface structure parameters and a possible change of mechanism of the H₂-evolution reaction than of a further increase of catalytic activity.

NOMENCLATURE

- TH: non-stoichiometric hydride (Ti/H = 1/1.7)
- RHE: reversible hydrogen electrode
- SMSE: saturated mercury sulphate electrode
- SEM: scanning electron microscopy
- EDS: energy disperse system
- T: temperature
- c.d.: current density
- pot.: potential
- b-value: slope of the Tafel-line (mV decade⁻¹)
- %: atomic per cent

INTRODUCTION

The large-scale production of hydrogen from water, meeting the technical and economic requirements for a viable hydrogen technology, is a crucial problem for a future energy system based on hydrogen as a universally applicable fuel.

To date, in particular, two electrochemical processes are of major importance for the technical generation of hydrogen: the chlor-alkali process and water electrolysis.

The R&D efforts were focused on: investigations of alternative non-noble metal catalysis and suitable methods for the production of active coatings on solid Ni, showing the required chemical and mechanical stability (adherence).

Operating conditions

The electrochemical measurements were carried out in 30-40% NaOH or KOH at temperatures ranging from 20 to 80°C.

Fundamental pathways of the H₂-evolution reaction

Overall process:

\[ 2\text{H}_2\text{O} + 2e^- \leftrightarrow \text{H}_2 + 2\text{OH}^- \]

(1) Volmer

\[ \text{H}_2\text{O} + e^- \leftrightarrow \text{H}_\text{ad} + \text{OH}^- \times 2 \]

Tafel

\[ 2\text{H}_\text{ad} \leftrightarrow \text{H}_2 \]

or:

(2) Volmer

\[ \text{H}_2\text{O} + e^- \leftrightarrow \text{H}_\text{ad} + \text{OH}^- \]

Heyrovsky

\[ \text{H}_2\text{O} + \text{H}_\text{ad} + e^- \leftrightarrow \text{H}_3 + \text{OH}^- \]

APPARATUS, EXPERIMENTAL AND MEASUREMENT TECHNIQUES

A standard electrochemical T-shaped cell was manufactured from polyacryl methacrylate. As a reference electrode a SMSE (Saturated Mercury Sulphate Electrode) was used. A Ni plate served as counter electrode; the stationary c.d./pot. measurements were carried out in hydrogen-saturated solution, whereas practical operation conditions were maintained during life tests.

Additional cyclic voltammograms were recorded for pretreatment and preliminary tests of electrodes.

Visible light and SEM (Scanning Electron Microscopy) were used in order to study the morphology of
the catalyst layers—including EDS (Energy Disperse System) analysis for a rough estimate of the composition of coatings.

**Preparation and activation procedures**

- Roughening of the electrode surface by volumetric cycling.
- Plasma-spraying of active coatings consisting of carbonyl-Ni and Raney alloy powder mixtures with successive activation in 20% NaOH.
- Coating of the electrode substrate with a surface area of 2 or 20 cm² respectively by painting or spraying a viscous suspension of catalyst powder mixtures in a solution of a suitable binder. The final coating was obtained by decomposition of the organic material and sintering the catalyst particles to the Ni-carrier at 1000°C in a hydrogen atmosphere, using a gas-tight furnace and an automatically controlled temperature program. The surface compositions of coated electrodes are given in Table 1. The surface-specific load of nickel and additives was in the range of 20 to 30 mg cm⁻².

**DISCUSSION OF THE RESULTS AND CONCLUSIONS**

Among various additives in Ni-based mixed catalysts (such as Ti, W, Mo, Ta, Zr, B, etc.), the best results were achieved with the binary mixtures with Ti and ternary catalysts containing Ti and B, providing low overvoltages (200-300 mV) at technical c.d. values (2-5 kA m⁻²). No definite increase of overvoltage was observed during long duration tests extended to several weeks.

1. The kinetic data obtained with smooth electrodes mainly reflect the influence of the electronic structure on the catalytic properties. High active surface areas are required, however, to meet the requirements under technical operating conditions (Fig. 1).

2. The catalytic activity can be distinguished from structural parameters by means of determination of activation energies (Table 1).

3. Virtually identical b-values (in general close to 120 mV (Table 1) are observed in a temperature range from 20 to 80°C (exception: electrodes with ternary Ni/Ti/B coatings indicating a variation of the transfer coefficients with temperature).

4. The electronic structure modified by combination of the two 4d metals Ni and Ti (different branches of the volcano curve) and hence the different bond strengths of Me-H is made responsible for the catalytic effect (Fig. 2).

5. Low Tafel slopes (b approx. 90 mV) at 80°C observed at Ni/Ti/B coatings indicate a change of mechanism probably due to a variation of composition of the

<table>
<thead>
<tr>
<th>Electrodes composition (at%)</th>
<th>Exchange current density (μA cm⁻²)</th>
<th>b-value at 20°C (mV c.d. decade⁻¹)</th>
<th>Activation energy (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni [100], smooth</td>
<td>6</td>
<td>120</td>
<td>45.1</td>
</tr>
<tr>
<td>Ni/TiH₂ [2:5/7:5]</td>
<td>50</td>
<td>115</td>
<td>11.3</td>
</tr>
<tr>
<td>Raney Ni</td>
<td>100</td>
<td>95</td>
<td>28.6</td>
</tr>
<tr>
<td>Ni/TiH₂/B [3:4/5:4.1]</td>
<td>70</td>
<td>100</td>
<td>75.7</td>
</tr>
</tbody>
</table>
surface layer and a temperature dependent behavior of the initially formed metal hydrides.

(6) No increase of polarization has been observed on coated electrodes during 1000-h tests at 80°C with current densities of 200 mA cm⁻².

(7) Commercially promising aspects can be seen in the low-cost materials and the relatively simple fabrication technology.

Future progress can be expected by optimization of the composition and the activation method (sintering process) of the active coatings.

REFERENCES