Short communication

Improved energy efficiency of the electrolytic evolution of hydrogen—Comparison of conventional and advanced electrode materials

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Abstract

With the idea to improve the efficiency of the electrolytic production of hydrogen by electrolysis, from water KOH solutions, the intermetallic Hf_2Co was investigated as cathode. This cathode was used single or in combination with ionic activators, and compared with several intermetallics previously investigated: Hf_2Fe, TiPt, and $PtMo_3$. A comparison with conventional cathode, nickel, was also evaluated. An significant upgrade of the electrolytic efficiency using intermetallics was achieved in comparison with conventional cathode materials. The influence of ionic activators on the process efficiency was significant, too.

The effects of those cathode materials on the electrolytic evolution of hydrogen were discussed in the context of transition metals features that issue from their electronic configuration.
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1. Introduction

With technology at its present stage, hydrogen is a very convenient secondary energy source at the end of the oil era and moreover a realistic long-term energy option as it enables energy storage, easy transport and efficient manipulation with energy, e.g. simple transfer to other forms of energy, primarily to the electrical one via fuel cells. Hydrogen, as a part of the water molecule, exists in practically inexhaustible quantities. In addition to that the water is the end product, if the hydrogen is used in the fuel cells as the energy medium, and is non-polluting for the environment. On the other hand, hydrogen production via water electrolysis promises to be of great future importance. One of the reasons for using this method is providing very clean hydrogen that does not need any refinement before usage. The electrolysis is also very perspective in the countries with cheap electrical energy, since the limiting factor for use the electrolytic method on the large scale (only 10% of all methods for hydrogen production belong to the electrolysis today) is well known high-energy consumption.

Hence, the development of high-efficiency electrolytic method is the one among numerous steps towards the improvement of the hydrogen economy with the idea to adjust all aspects of 'hydrogen philosophy' with sustainable development.

The main idea of this work was the attempt to increase the electrolytic process efficiency by using intermetallics of transition metals as cathode materials for hydrogen produc-

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tion in combination with in situ activation by ionic activator, the following compounds combination: 1×10^{-3} mol dm^{-3} of [Co(en)$_3$]Cl$_3$ complex and 1×10^{-2} mol dm^{-3} of Na-molybdate, in the standard electrolyte (30 wt.% KOH). It was found [1] that this ionic activator exhibits the best electrocatalytic effects.

1.1. Theoretical consideration

The electrocatalytic activity for the hydrogen evolution reaction (HER) and the bonding effectiveness of transition metals and its intermetallics are in close correlation. They are a periodic function of the atomic number within three long transition metal periods [2]. The electrocatalytic features obey volcanic curves with a maximum at about d^8-electrons [2–4].

Brewer's high temperature thermodynamics [5–7] suggests that the intermetallic phases with very strong bonds, were made by bonding hypo- with the hyper-d-electronic transition metals, where in accordance with generalized Lewis acid–base reaction, there is a transfer of electrons from the orbital with paired d-electrons onto the empty or half-filled d-orbital. It has been shown [8,9] that more exposed d-orbital in the region from 3d to 5d correspond to the stronger cohesive and therefore weaker adsorptive bonding, resulting in higher electrocatalytic activity for the HER.

In spite of the fact that the elctrocatalytic activity is in close correlation with the electronic configuration of individual metals and/or their intermetallics, some of high electrocatalytic activities could additionally be explained on the basis of three-dimensional hydridic features of composite electrocatalysts, and the ability to absorb certain amount of hydrogen [10–12].

The time differential perturbated angular correlation (TD-PAC) method results clearly indicate that hydrogen preferentially fills a specific type of interstitial site. The presence of hydrogen drastically changes the magnetic properties. The Mossbauer spectra and the susceptibility measurements for both compounds show that the hydrides have a disordered (spin-like) magnetism [13].

Polycrystalline compounds, Hf$_2$Fe and Hf$_2$Co, are Pauli paramagnetics with the same type structure. These intermetallics belong to the group of binary systems formed between hypo- (Ti, Zr and Hf) and hyper-d-transition metals (Fe, Co, Pd, Pt). Among other reasons, they have been investigated as systems interesting for hydrogen storage, since they are able to form hydrides in hydrogen – metal atom ratios $H/M \geq 1$ at rather low temperatures ($T \to 300\,°C$) and high pressures (>1 kPa) [14].

Hf$_2$Fe and Hf$_2$Co crystallize in the cubic Ti$_2$Ni type structure (space group Fd3m) with 96 atoms per unit cell. The 32 Fe atoms are in positions 32e, the 64 Hf atoms are distributed on the two positions, 16c (Hf1) and 48f (Hf2). The unit cell constants are for Hf$_2$Fe: $a = 12,033$ Å and for Hf$_2$Co: $a = 12,084$ Å, both nonannealed.
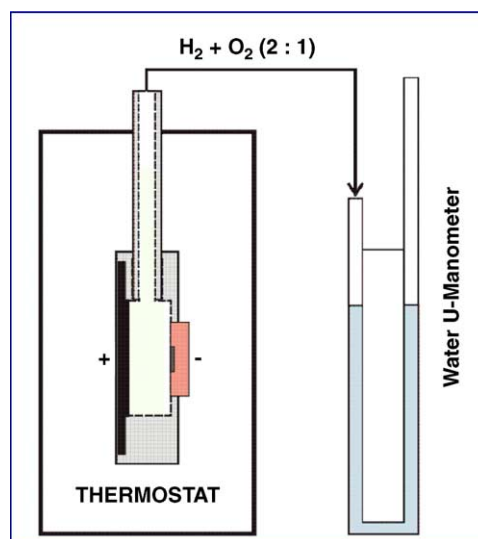

Fig. 1. Experimental set up: the electrolytic cell and the water filled U-tube manometer, used for measuring the catholically evolved amounts of hydrogen.

2. Experimental

All experiments have been carried out in a Plexiglas-made electrolytic cell, Fig. 1, with an interelectrode distance of 10 mm. The cathode made of intermetallic materials was attached on one side, and the anode (Ni) on the other. The latter was a round shaped electrode of 29.5 mm in diameter ($P = 683.5$ mm^2), also used in our previous experiments [1].

The cathodes used were compact and homogeneous intermetallics, prepared by specific thermometallurgical procedure, polished before use.

The electrolyte in the process was 30 wt.% KOH, which corresponds to typical industrial conditions for water electrolysis.

The amount of cathodically evolved gasses (hydrogen + oxygen, 2:1) during certain time was determined using a water filled U-tube manometer. Time (t) of evolution of certain volume of hydrogen, along with overall voltage through the cell (U) were recorded for specified overall current through the cell (I) and temperature, in order to calculate corresponding energy consumption.

The experimental conditions were as follows: current density range from 30 to 500 mA cm^{-2} and temperatures range from 256 to 348 K. The experiments were maintained by thermostat/cryostat, power supply and measuring electronics (computer controlled galvanostat) as was described elsewhere [1,15,16].

3. Results and discussion

In the hydrogen electrode reaction, $2H^+ + 2e^- = H_2$ that is a heterogenous catalysis, an electrode material acts as the catalyst. Its activity is closely related to the electronic

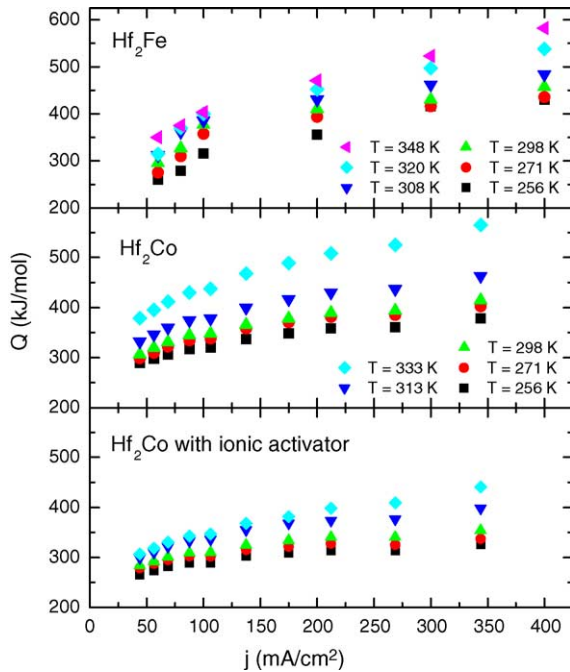Fig. 2. Energy consumption per one mole of hydrogen evolved, as a function of current density at different temperatures. Cathodes: Hf_2Fe and Hf_2Co in standard electrolyte and in standard electrolyte with added ionic activators; anode: nickel.

configuration of these materials. Energy requirement for the electrolytic hydrogen evolution process is a measure of the electrocatalytic activity of electrode materials and is calculated using relation:

$$Q = IUt$$

where the units specified are defined in Section 2.

The results obtained are presented in Fig. 2. and in the three-dimensional graph for explicit insight, Fig. 3. It shows an expected type of dependence, increase of the energy consumption with the increase of the current density and an inverse temperature influence. The effects of ionic activators on
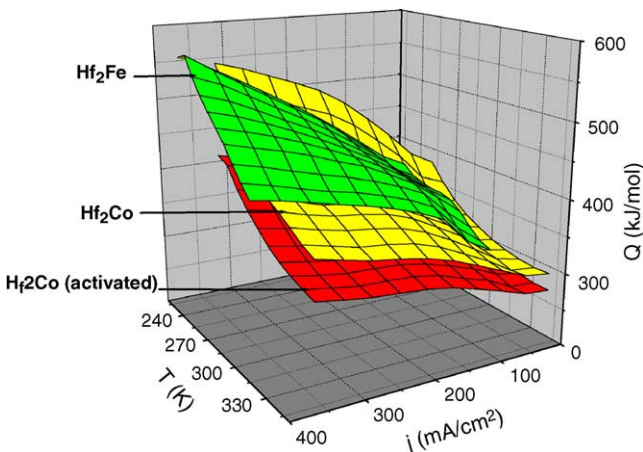

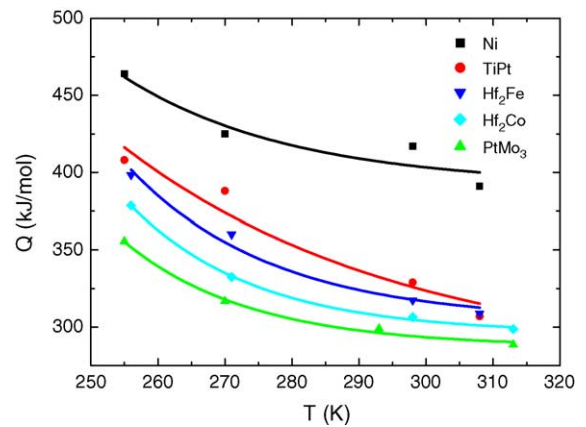Fig. 3. 3D-diagram constructed using all data from Fig. 2.

Fig. 4. Comparison of the energy consumption per 1 mol of hydrogen evolved as a function of temperature, at the current density of $30\,mA\,cm^{-2}$, at different cathodes.

the process efficiency are also visible, i.e. in their presence the energy consumption decreases. The possible mechanism through which ionic activators increase electrolytic efficiency that is decrease energy requirement, is discussed in our previous work [1].

On the basis of these results, the functional dependence of energy consumption and temperature, and the comparison between several intermetallics, recently investigated in our works [16,17], and Hf_2Co, for the current densitiy of $30\,mA\,cm^{-2}$, is shown in Fig. 4. The comparison with conventional cathode, nickel, is presented in this figure, too.

Conclusion is that Hf_2Co exhibits the better electrocatalytic effect than Hf_2Fe but inferior compared to $PtMo_3$. The intermetallics used could be ordered as follows, according to their electrocatalytic activity (the energy requirement is in the inverse order):

$$PtMo_3 > Hf_2Co > Hf_2Fe > Ti\text{–}Pt > Ni.$$

The activation of the process by using ionic activators in situ exhibits an additional effect.

In our further work, a hybridization effects among electronic orbitals will be treated using Wien97 programs in order to understand subtle differences in better production of hydrogen at Hf_2Co in comparison with Hf_2Fe, suggesting 3d–5d electron transfer mechanisms among the nearest ions in the unit cells.

The results presented in this work could be interpreted on the basis of the circumstances exposed in the theoretical consideration.

4. Conclusion

The pronounced electrocatalytic effects of the intermetallics and ionic activators are in close correlation with d-electronic configuration of single transition metals and/or their mutual combinations.

In order to make the better interpretation of Hf_2Fe and Hf_2Co different electrocatalytic activities, further experiments with these hydrides (Hf_2FeH_x and Hf_2CoH_x, $x \rightarrow 1$–5) are required to obtain the more precise information on hydrogen configurations [18,19].

Acknowledgements

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