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INTERMETALLICS – ADVANCED CATHODE MATERIALS IN THE ELECTROLYTIC PRODUCTION OF HYDROGEN

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Abstract

The intermetallics, Ti-Pt, Nb-Pd (80%Nb), Pd-Ta, Nb-Pd (65% Nb), Zr-Pt, Hf₂Fe and PtMo₃, of transition metals have been investigated as cathode materials for the electrolytic hydrogen evolution in an attempt to increase the electrolytic process efficiency. These materials were compared with conventional cathode, Ni. An significant upgrade of the electrolytic efficiency using intermetallics was achieved.

The effects of those cathode materials on the process efficiency were discussed in the context of transition metal features that issue from their d-electronic configuration.

Introduction

Hydrogen is a very convenient secondary energy source at the end of the oil era. As recent technology progress makes hydrogen a realistic long-term energy option with little or no pollution, development of new methods and improvement of conventional technology for its production is important. The limiting factor for use the electrolytic method on the large scale is well known high energy consumption. In spite of this, hydrogen production *via* water electrolysis promises to be of great future importance. So, the development of high-efficiency electrolytic method represents a step 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 to investigate the water electrolysis efficiency using different intermetallic phases of transition metals as cathodes. This specific combination of transition metals (hypo d- electronic and hyper d-electronic) demonstrates a well-pronounced electrocatalytic effect. Also, some of high electrocatalytic activities could be explained on the basis of three-dimensional hydridic features of composite electrocatalysts and their ability to absorb certain amount of hydrogen [1, 2].

Experimental

The electrolytic cell was made of plexiglass, having the cathode made of intermetallic materials attached on one side, and the round shaped anode (nickel) on the other. The amount of gases evolved during certain time was determined using a water filled U-manometer. The standard electrolyte was 30 wt.% KOH water solution. The experimental conditions were as follows: Current density ranges from 15 to 700 mA/cm². The applied temperatures were from 256 K to 348 K (from -17 °C to +75 °C).

The intermetallics used as cathodes were as follows: 1. Ti-Pt, 2. Nb-Pd (80%Nb) 3. Pd-Ta, 4. Nb-Pd (65% Nb), 5. Zr-Pt, 6. Hf₂Fe and 7. PtMo₃, while nickel was used as the anode material in all investigated systems. Thus, the anode contribution was always the same. In this way we were able to see the role of cathode materials in energy consumption, as a function of the overall current density and voltage.

Results and Discussion

The hydrogen electrode reaction, $2\text{H}^+ + 2\text{e}^- = \text{H}_2$, is a heterogeneous reaction where an electrode material acts as the catalyst. The activity is closely related to its electronic configuration.

The energy consumption was determined using the relation: $Q = I U t$, where I (A) and U (V) are overall current and voltage through the cell, while t (s) is the time of evolution of a certain volume of hydrogen. The results obtained for Ti-Pt and PtMo₃ were compared with those for Ni in Fig. 1, also obtained in our laboratory by the same method [3]. It might be concluded that the intermetallics are more efficient than Ni as it was expected, and PtMo₃ is the best electrocatalyst among them.

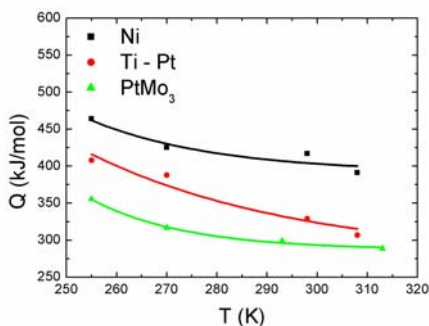


Fig. 1. Comparison of the Ti-Pt and PtMo₃ cathodes to Ni cathode at current density of 30 mA/cm².

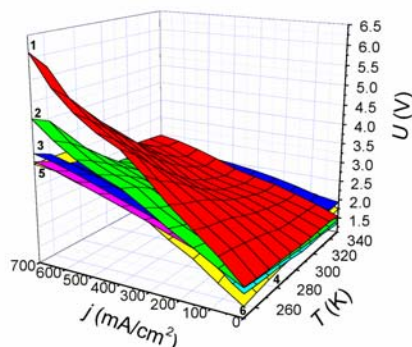
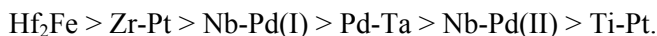


Fig. 2. Cell voltage as a function of current density at different temperatures for investigated intermetallics.

The overall voltages through the cell, U (V), as a relative measure of the energy consumption, at different current densities and temperatures for investigated intermetallics: 1) Ti-Pt, 2) Nb-Pd(II), 3) Pd-Ta, 4) Nb-Pd(I), 5) Zr-Pt, 6) Hf₂Fe, are presented in three-dimensional diagram (Fig. 2). On the basis of these data the intermetallics used could be ordered as follows, according to their electrocatalytic activity (the energy requirement is in the inverse order):



The use of vacant d-orbitals of Zr, Nb or Hf by the nonbonding electrons of Pd and Pt could optimize the employment of available orbitals and electrons in the hydrogen evolution reaction. In the case of Zr-Pt intermetallic the expected transfer of

d- electrons is from platinum (d^7sp^2) to low-lying vacant orbitals of zirconium and these intermetallics should be unusually stable. Further, since the strength of d-electron bonding increases quite markedly from 3d to 4d, and substantially from 4d to 5d levels, the stability of intermetallics and consequently electrocatalytic activity, could be rather low when only 3d-orbitals are involved, being higher when 4d orbitals and highest when 5d orbitals are employed [4]. This can explain why the Zr-Pt combination is better than the Ti-Pt one. This explanation and the fact that Hf_2Fe intermetallic absorbs large amounts of hydrogen [2], could further explain the better electrocatalytic activity of this material.

Conclusion

Several intermetallic combinations of transition metals were used as cathode materials in the electrolytic evolution of hydrogen from alkaline aqueous solutions. In comparison with the conventional cathode; Ni, an upgrade of the electrolytic effect using these intermetallics has been achieved. These intermetallics have shown significant electrocatalytic effects.

The pronounced electrocatalytic effects of these intermetallics were discussed in the context of the mutual interaction of their d-orbitals. Generally, all those effects connected with the electrocatalytic activity, are in close correlation with d-electronic configuration of single transition metals and/or their mutual combinations.

Acknowledgments

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