

Fig. 1. Values of specific energy and specific power for various types of cells

This system is characterized by much more greater energy capacity (60–80 Wh/kg) than nickel-cadmium cells (30–50 Wh/kg), commonly used until recently, or traditional lead-acid batteries (25–40 Wh/kg). Relatively low internal resistance of Ni-MH cells enables to obtain discharging current of quite high density, which is accompanied by the resistance to repeated charging and discharging (even to 2000 cycles). Moreover, Ni-Cd batteries has been withdrawn from the European market due to content of toxic cadmium.

One of the more important applications of hydride cells is their use in hybrid electric vehicles, which are powered by combustion and electric engines or by an electric engine powered from fuel and hydride cells. Fig. 1 shows the values of specific energy (Wh/kg) and specific power (W/kg) of selected cells. The cell power is mirrored in the current density obtained. The highest energy capacity and power is characterized by lithium-ion batteries, although there is no system that is characterized by both the highest capacity and power. The lithium-ion cells of the highest power possess the capacity comparable with that of hydride cells. Moreover, the cost of energy unit stored in a lithium-ion cell is several times greater in comparison with a hydride cell.

Fig. 2 illustrates the operation scheme of a nickel-hydride battery, where a metallic hydride serves as the anode and NiOOH serves as the cathode. In the investigated Ni-MH cell a typical AB5 alloy (LaMmNi₄,1Al₀,2Mn₀,4Co₀,45) will be used together with 6M KOH electrolyte, as in the commercial batteries.

In order to make the working parameters of our cell closer to those of high-power lithium-ion cells we are going to introduce to the hydride cell an asymmetric electrochemical capacitor operating at the same voltage as the hydride cell due to the same anodic reaction of absorbed hydrogen oxidation. The common positive electrode of the cell will be NiOOH. The electrochemical capacitor will be obtained by electrodeposition of hydrogen-absorbing Pd/Pd alloy layer on conducting porous carbon (CPC).

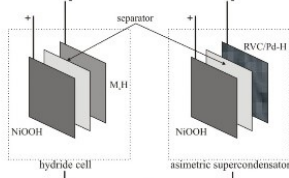
The processes occurring in the electrochemical capacitor Pd(alloy)/CPC and in the hydride cell Ni-MH involve the same reactions of hydrogen electrosorption into and desorption from the metal, although the processes in palladium and its alloy are much faster than in less noble components of the AB5 alloy.



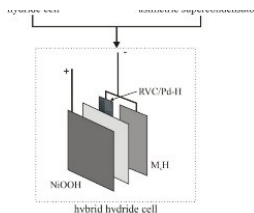
Fig. 2. Scheme of reactions occurring in a nickel-hydride battery during charging and discharging

Thin Pd and Pd alloy layer have been examined as the electrode materials for electrochemical capacitors with respect to the specific capacity and power. The systems of Pd and Pd-Rh with conducting porous carbon have been patented. Our latest studies have revealed that a Pd-Ru alloy (with 1% of Ru) exhibits hydrogen capacity by 20% greater than pure Pd. On the other hand, the investigations on binary Pd alloys for the electrochemical capacitor have shown that platinum is the best catalyst of hydrogen oxidation process.

The electric contact between Pd/Pd alloy system and the AB5 alloy will be realized by:



- direct placement of the AB5 alloy on a matrix made of Pd deposited on a hydrogen-neutral substrate, such as Ni and CPC
- formation a composite material from the AB5 ally and Pd (as the negative electrode), which will be incorporated into the pore of CPC. In order to verify the above idea a preliminary experiment has been carried out with the use of a cell containing a thin-layer AB5 electrode and Au grid plated with a thin Pd layer (ca. 1 μm), connected in parallel. The gold substrate was



chosen due to its inertness in hydrogen sorption processes. 6M KOH was used as the electrolyte. The comparison of discharging current densities obtained in the very first seconds of hydrogen oxidation lead to the conclusion that due to the contribution of the Pd-H system the cell power increased by ca. 50% , although the total mass contribution of Pd in the hybrid cell was only ca. 0.36%.

Fig. 3. Scheme of a hybrid Ni-MH cell

This preliminary experiment has confirmed all the main assumptions of the project, i.e.:

1. Hydrogen oxidation from Pd-H and AB5-H systems proceeds in the same potential range
2. Hydrogen oxidation from Pd is much faster than from the AB5 alloy due to the differences in the overvoltage and the rate of diffusion of hydrogen in various materials.
3. The use of a hybrid system composed of different hydrides results in cell power increase (increase in discharging current).

In our planned investigations we expect other systems with Pd alloys with Rh and Ru to have a greater effect than pure Pd on the increase in discharging currents obtained from the hybrid cell. A very interesting effect might be the influence of platinum additive to Pd alloys with Ru and Rh due to the catalytic effect on the rate of hydrogen oxidation.

A target system in our investigations will be a composite material: AB5-type alloy with an additive of Pd alloys with the metals that increase the absorption capacity (Rh, Ru) and facilitate hydrogen electrooxidation (Pt). Conductive porous carbon (CPC) plated with a thin Pd-based layer will serve as a matrix and current collector.

The project is a pioneer approach to the research on the methods of energy conversion and storage. A new type of a hydride cell (not known in the literature) will be constructed, in which the negative electrode (serving as the anode during discharging) will consist of a hybrid system of transition metal hydride-alloy components and an electrochemical capacitor composed from platinum metal hydrides.

The AB5-Pd(Rh, Ru, Pt)/CPC system will be optimized in the aspect of obtaining the maximum current power from absorbed hydrogen oxidation during cell discharging. During charging process hydrogen will be inserted into the anodic electrode system, first do the capacitor electrode, from where the charge will be continuously transferred into the AB5 electrode mass of higher capacity. Numerous fundamental studies on that system are necessary.

If our idea of the composite hybrid hydride cell was applied in practice in the form of new nickel-hydride batteries, our pioneer results presented in scientific publications could serve as a primary source of knowledge and a literature basis for future investigations and constructors.

REFERENCES

1. A. Czerwi ski, "Accumulators, batteries and cells" WKŁ Warszawa, 2005.
2. G. Wójcik, M. Kopczyk, H. Drulis, M. Bełtowska-Brzezinska, Wiad. Chemiczne, 49 (1995) 5.
3. A. Czerwi ski, Z. Rogulski, J. Dłubak, A. Gumkowska, M. Karwowska „Perspectives of hydride cells (Ni-MH)", Przemysł Chemiczny, 88/6 (2009) 642
4. A. Czerwi ski, A. urowski, M. Łukaszewski, „Electrode for electrochemical capacitor" Patent RP 204948, 2010
5. J. Wróbel, K. Wróbel, J. Lach, J. Dłubak, P. Podsadni, Z. Rogulski, I. Paleska, A. Czerwi ski, „Application of reticulated vitreous carbon in electrochemical power sources" Przemysł Chemiczny, 93/3(2014) 1000
6. U. Koss, K. Hubkowska, M. Łukaszewski, A. Czerwi ski „Palladium alloys with rhodium and ruthenium as hydrogen-absorbing materials of high absorption capacity", Przemysł Chemiczny, 94/3, 2015, 2912 pages here