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INFLUENCE OF EXTERNAL MAGNETIC FIELD ON THE ELECTROLYTIC HYDROGEN EVOLUTION ON DIFFERENT CATHODE MATERIALS

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Abstract

The correlation between magnetic properties of cathodic materials on the evolution of hydrogen and the separation factor was found. The cathodes were pure Ni and cathodes with the electrocatalytic coatings of following compositions: Ni-Mo (70-30%), Ni-V (70-30%), Co-Mo (70-30%) and Fe-Mo (60-40%), on Ni substrate. The electrolyte is standard electrolyte (30% KOH) and electrolyte activated with Co-complex [1].

Introduction

High separation factor was received by using an iron electrode prepared in the magnetic field [2]. Namely, the iron film was electrodeposited in a magnetic field and the obtained separation factor α was 12.3, that is much higher than of conventional mild steel electrode ($\alpha = 5-9$). Further, when new deuterium separation system, using fuel cell, is applied with this new iron electrode the energy requested is significantly reduced [3].

In our previous papers [3-7] water electrolysis in alkaline solutions has been studied as the method for hydrogen production and hydrogen isotopes (D,H) separation. On different kind of cathode materials, single transition metals and/or Brewer hypo-hyper-d-electronic intermetallics of transition metals, significant increase in separation factors were obtained when *in situ* activation with tris-(ethylenediamine)Co(III) chloride complex, tris(en), was applied [3]. Further, ionic activator used have shown significant electrocatalytic effect, that means energy saving per mass unit of evolved hydrogen from alkaline aqueous solutions was reduced (in some cases beyond 10%) [7]. *In situ* activation with the other complex, tris-(trimethylenediamine)Co(III) chloride complex, tris(ten), have given much better result in the case of separation efficiency. It undoubtedly means that all those activated surfaces of the electrodes approved the electrocatalytic effects that, as it is well known, issue from their d-electronic configuration.

The aim of the present work was to find the correlation between magnetic properties of some cathode materials (singly transition metals and/or their intermetallics in standard electrolyte and in activated one) and their efficiency in hydrogen evolution and hydrogen isotopes (H/D) separation processes.

Results and Discussion

The experimental obtained values of magnetisation, M , at the applied magnetic field of 6000 Oe were compared with previous received values of separation factors, α . It was found that the magnetisation increased on those materials which exhibit the increased values of separation factors. The maximum value of magnetisation and separation factor was achieved by cathode made of nickel ($M = 51.14$ emu/g and $\alpha = 7.6$, respectively) and minimum is for nickel cathode with thermochemically deposited iron and molybdenum, Fe-Mo (60-40%) ($M = 45.20$ emu/g and $\alpha = 4.0$, respectively).

During the electrolysis with addition of following ionic activators: tris(ethylenediamine)Co(III)-chloride, tris(en), and tris(trimethylenediamine)Co(III)-chloride, tris(ten), into the electrolyte, the deposition of fine black powder on cathode surface occurred. Therefore, we measured the magnetisation of nickel cathode with deposit and of the same deposit removed from cathode surface. In all cases the separation factors were measured as well. On the basis of the results obtained, when *in situ* activation with tris(en) complex was applied, we concluded that the separation factor and magnetisation of activated nickel cathode is increased compared with non-activated one, magnetisation for about 4% and the attained increase in separation factor was about 32 %.

The best results of separation factor and magnetisation were achieved when activation with tris(ten), as activating complex, was used. During the electrolytic process, black deposit was formed on nickel cathode from complex added into the electrolyte. Pure nickel has magnetisation of 51.14 emu/g and the value of it for deposit sample is 63.02 emu/g. It means that removed deposit from electrode surface has 23 % bigger value of magnetisation than pure nickel, and separation factor increase is 97 %.

The presentation of separation factors as a function of magnetisation for different cathode materials is given in Fig. 1. The linear function of dependence, α vs. magnetisation, was obtained.

It is important to mention that, in accordance with our previous investigation, the energy consumption was improved, as well. So, for pure nickel the energy requirement was $510.3 \text{ kJ mol}^{-1}$ and in activated system the decreased value of $487.7 \text{ kJ mol}^{-1}$, was obtained [1]. Therefore, in the consideration of the improvement of separation efficiency the decrease in energy requirement in the electrolytic hydrogen evolution process has its significant contribution.

Emphasizing the role of the hydrogen bonds we do hope to introduce a more suitable approach in understanding and controlling the influence of the deposit on the improvement of hydrogen evolution efficiency. Obtained magnetic properties of deposit, and generally speaking influence of magnetic field, is not well known especially if we take in consideration influence on hydrogen reaction.

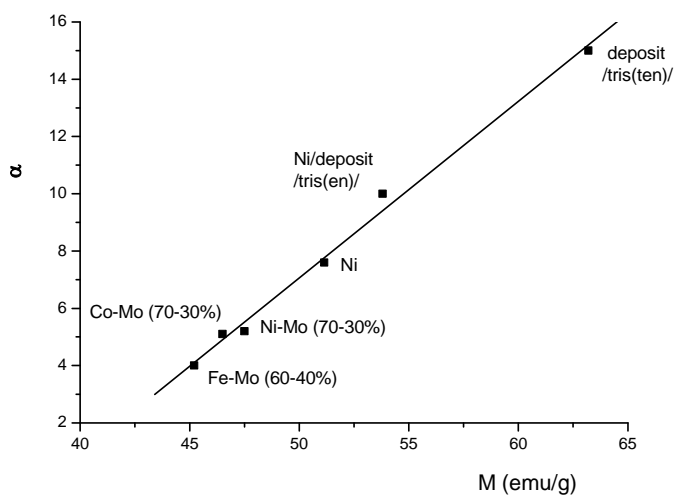


Fig. 1. Separation factors as a function of magnetization for different cathode materials singly and/or in the presence of ionic activators.

Conclusion

Magnetic properties of cathode materials and cobalt deposit on nickel surface is evident and it has obvious influence and increase on separation factor i.e. increase evolution of hydrogen during electrolyses in water KOH solution. The obtained correlations between magnetic properties and electrocatalytic activity of the investigated cathode materials issue from their d-electronic configuration.

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References

- [1] Dragica Lj. Stojić, Tomislav D. Grozdić, Vojislav V. Spasojević, Ana B. Umićević and Sofija P. Sovilj, *Influence of magnetic behavior of cathodic surface on deuterium separation factor*, *Electrochemistry Communications*, 2007, **9**, 2408-2411.
- [2] H. Matushima, T. Nohira, Y. Ito, *Improved deuterium separation factor for the iron electrode prepared in a magnetic field*, *Electrochimica Acta*, 2004, **49**, 4181-4187.
- [3] H. Matushima, T. Nohira, T. Kitabata, Y. Ito, *A novel deuterium separation system by the combination of water electrolysis and fuel cell*, *Energy*, 2005, **30**, 2413-2423.