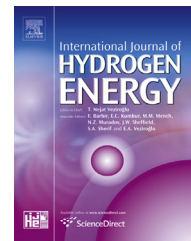


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Interaction mechanism of hydrogen storage materials with layer-by-layer applied protective polyelectrolyte coatings

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ABSTRACT

Metal hydrides are promising compounds for the storage of hydrogen especially in the transport sector. Their high reactivity with moisture and difficult handling in ambient atmosphere prevents their easy application in tanks and thus the market penetration of this very promising and clean technology. In the present work we investigated the way to protect sodium borohydride with organic polyelectrolytes like polyethyleneimine (PEI) and dicarboxy terminated poly(acrylonitrile-co-butadiene-co-acrylic acid) (PABA) with emphasis on the interaction of those polyelectrolytes with the SBH. The polyelectrolytes protect SBH either by electrostatic adsorption or by reacting with it, depending on the reactive groups present in their structure. PABA undergoes only an electrostatic interaction with the SBH substrate. PEI on the other hand interacts chemically with the SBH substrate and forms complexes with groups on the SBH surface. Both polyelectrolytes can be applied in a layer-by-layer approach on the SBH in order to protect it. Regarding the best order of the layer application XPS results yield that the formation of the boron-amino-complexes between the PEI and the SBH is independent of the order in which the PABA and PEI layers are applied. However, the rearrangement of the SBH surface groups due to the application of the PEI films has been found to be considerably influenced by the order of application. The effect of a PEI film has been mostly compensated by the subsequent application of a PABA film, while the application of PEI had a much larger influence on the surface of a PABA coated SBH sample. Thus, the best order of the layer application with respect to the application according to XPS is to deposit the PEI layer at first and the PABA layer afterwards.

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Introduction

The prospective sources of chemical energy for a variety of applications will most probably be based on hydrogen [1,2] and it is expected that hydrogen will play the key role especially in the transport area. The storage of hydrogen though remains as one of the most critical tasks prior to establish a hydrogen economy and it still has not been overcome [2].

The difficulties in storing hydrogen originate from its low density and low critical temperature. On one hand, there are different physical approaches for hydrogen storage that are currently investigated, including compressed or liquefied hydrogen in tanks [1], adsorption on activated carbon [3,4] and carbon nanotubes [4,5], hydrogen-absorbing alloys [5], or metal-organic frameworks [6].

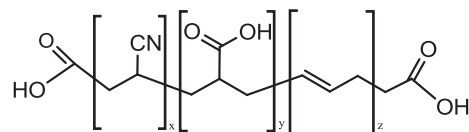
On the other hand, different chemical storage methods and materials are being explored, such as inorganic hydrides including simple metal hydrides as NaH [7], LiH [6] or MgH₂ [8] as well as alanates like NaAlH₄ [9] or metal borohydrides as LiBH₄ [10] and NaBH₄ [5,11]. Furthermore, some approaches use amides [6] or organic hydrogen-enriched compounds (methylcyclohexane, decalin) [12,13].

A decreased grain size of such complex metal hydrides, structural defects introduced via ball-milling and especially the addition of nanometric elemental metals have been found to enhance the hydrogen desorption rates significantly [14,15].

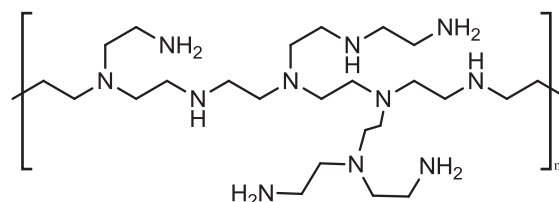
The hydrogen content of complex metal hydrides is most commonly released by hydrolysis [16], while it is also possible to reversely release the hydrogen via thermal desorption [17].

The complex metal hydrides exhibit a much easier handling than the other storage approaches. Amongst these complex metal hydrides, the NaBH₄ is considered to be the most attractive hydride for its easy synthesis [2]. However, all of these materials suffer from severe ageing after long times of exposure to air or other humid environments by forming surface oxides which act as kinetic barriers for hydrogen desorption [18]. In many cases it is even not possible to work with those materials in ambient atmosphere. Thus, the complex metal hydrides as hydrogen storage materials have to be protected from direct contact with the surrounding atmosphere making possible their easy and safe handling for long time, for example during packaging of these materials in storage tanks and devices. This protection can be done e.g. via interfacial polymer precipitation induced by solvent evaporation. Sodium boron hydride has been successfully protected for example with a polystyrene shell by co-precipitation. This shell provides a hydrophobic barrier for water diffusion into the container interior [19]. Furthermore, multiple polyelectrolytes can be employed to build up the protecting shell from alternating anionic and cationic polyelectrolytes. For best results, these shell materials have to be water impermeable but H₂ permeable.

In the present study we used alternating polyelectrolyte layers of polyethylenimine (PEI) and dicarboxy terminated poly(acrylonitrile-co-butadiene-co-acrylic acid) (PABA) as protecting shell (see Fig. 1) and investigated its influence on the stability of sodium borohydride (SBH). Thus, we extend the preliminary results on the thermal stability and the hydrogen release of SBH protected by polyelectrolyte shells [17], where



Poly(acrylonitrile-co-butadiene-co-acrylic acid),
dicarboxy terminated: PABA
[M ~ 3.600 g/mol]



Polyethylenimine, branched: PEI
[M ~ 10,000 g/mol]

Fig. 1 – Chemical formulae of the used polyelectrolytes PEI and PABA.

we found both polyelectrolytes to enhance the hydrogen release. This was found to be most significant for PEI, which also effectively lowered the hydrogen release temperature. The PABA coating slightly increased the hydrogen release temperature, but improved the stability of the SBH substrate as well.

As reported in the literature [2,20], the layer-by-layer method effectively protects sensitive hydrogen storage materials like SBH. PABA and PEI form stable complexes with SBH and the formed shell is impermeable to polar compounds like water, thus effectively protecting the hydrogen storage material. In doing so, ζ -potential measurements revealed an electrostatic interaction between PABA and SBH leading to very stable films, while PEI would not directly stick to the SBH by electrostatic interactions [2].

A previous study proved the formation of stable films of PABA as well as PEI on SBH. These films appeared to completely cover the surface of the SBH grains, while exhibiting a rough surface structure [17]. However, these works have shown the protection of the hydrogen storage material in a more or less empirical way. In the course of the present work, the interaction of the polyelectrolytes with SBH as well as with each other when they are applied on SBH in an alternating way has been investigated by means of X-ray photoelectron spectroscopy (XPS), nuclear magnetic resonance spectroscopy (NMR), and Fourier transform infrared spectroscopy (FT-IR).

Results

In the following sections we present results obtained from measurements on the used materials performed by means of the experimental methods presented in the experimental section.

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