



The influence of protecting polyelectrolyte layers on the temperature behavior of NaBD₄

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The use of NaBH₄ as a hydrogen storage material suffers to some extent from its deficient stability against chemicals and degradation at elevated temperatures. This disadvantage can be overcome by the use of polyelectrolytes as protective layers. Furthermore, the coating of NaBH₄ with polyelectrolytes significantly enhances the release of hydrogen from the storage material. In this work, the influences of polyethyleneimine (PEI) and poly(acrylonitrile-co-butadiene-co-acrylic acid), dicarboxy terminated (PABA) as protective polyelectrolyte coatings have been investigated on deuterated sodium borohydride, thus being able to determine hydrogen release from the polyelectrolyte and the hydrogen storage material. The release rates have been investigated by temperature-programmed desorption measurements of significant species as preliminarily identified by mass spectrometry. Furthermore, the geometrical structures of the polyelectrolyte films were characterized by confocal laser scanning microscopy studies prior and posterior to the temperature treatment.

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1 Introduction

Hydrogen is the most attractive element as a source of chemical energy^{1,2} and its storage is one of the most important tasks for the development of a hydrogen economy. Hydrogen is expected to play a key role in this area, especially in the transport sector. However, storage remains one of the most critical issues, which has to be solved before a technically and economically viable hydrogen economy can be established. In fact, a hydrogen economy will be difficult to achieve without effective storage systems.²

Storing hydrogen is difficult, because of its low density and low critical temperature. Currently, there is a number of different approaches for hydrogen storage, including compressed or liquefied hydrogen in tanks,¹ adsorption on activated carbon^{3,4} and carbon nanotubes,^{4,5} hydrogen-absorbing alloys,⁵ inorganic hydrides including NaBH₄,^{5,6} NaH,⁷

LiH,⁶ NaAlH₄,⁸ MgH₂,⁹ LiBH₄,¹⁰ and organic hydrogen-enriched compounds (methylcyclohexane, decalin).^{11,12}

A simple approach for the protection of hydrogen storage materials (HSM) is based on interfacial polymer precipitation induced by solvent evaporation. Sodium borohydride is successfully protected for example with a polystyrene shell by co-precipitation. This shell provides a hydrophobic barrier for water diffusion into the container interior.¹³

It is possible to use more than one polyelectrolyte in order to form the protecting shell by using alternating anionic and cationic polyelectrolytes.

The shell material finally formed by the polyelectrolyte(s) has to be water impermeable but H₂ permeable. In the present study we investigated the influence of protecting polyelectrolyte layers on the temperature behavior of deuterated sodium borohydride (NaBD₄). It is of particular interest to investigate the thermal stability as well as the hydrogen release of polyelectrolyte shell protected hydrogen storage materials.

As reported in the literature^{2,14} the layer-by-layer is an effective method for the effective protection of sensitive hydrogen storage materials and especially NaBH₄. PABA and PEI form stable complexes with NaBH₄ and the formed shell is impermeable to polar compounds like water, thus effectively protecting the hydrogen storage material.²

2 Experimental details

For the protection of the deuterated sodium borohydride (NaBD₄ supplied by Sigma-Aldrich purum p.a., ≥96%) we used

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the well known layer-by-layer approach first reported by Decher *et al.*¹⁴

Until now, the application of this technique has been limited to the use of water-based solvents for nanofilm fabrication. Different groups like Dobbins *et al.*¹⁵ or Borodina *et al.*^{2,13} have developed a detailed procedure how to use the layer-by-layer method with organic solvents in order to prepare protective shells on NaBH₄. In the present study we used this methodology in order to prepare a protective shell made of polyethyleneimine (PEI) and poly(acrylonitrile-*co*-butadiene-*co*-acrylic acid), dicarboxy terminated (PABA) on deuterated sodium borohydride.

16 mg of the polyelectrolyte have been dissolved in 4 ml of dichloromethane (DCM) and 200 mg of the micrometer sized NaBD₄ were incubated in this solution for 5 min. Afterwards the polyelectrolyte solution has been decanted, the remaining NaBD₄ was filtrated and washed two times with 4 ml of DCM in order to remove loose-packed residuals of the polyelectrolyte. Afterwards the prepared NaBD₄ was dried overnight in a desiccator over CaCl₂.

We used NaBD₄ in order to be able to better follow the hydrogen release during the stability studies. By using NaBD₄ we can detect released D₂ more easily than H₂ for the temperature-programmed desorption (TPD) studies and thus discriminate contributions from the HSM and residual gas in the vacuum chamber.

For the TPD investigations, pellets with 13 mm diameter were prepared using 50 mg of NaBD₄ by uniaxially pressing it with 10 kN and immediately transferred into the vacuum transfer chamber. An ultra high vacuum (UHV) apparatus with a base pressure of 5×10^{-11} hPa, which has been described in detail previously,^{16–20} was used to carry out the experiments on the temperature stability. A differentially pumped quadrupole mass spectrometer system equipped with a Balzers QMG 422 and a linear motion feed for positioning its faceplate right in front of the sample was used for the detection of possible reaction products during the heating process.

The determination of eligible fragments was conducted using a Varian 320 MS TQ mass spectrometer equipped for electronic ionization (EI) as well as chemical ionization (CI), both at tunable excitation energies.

Confocal Laser Scanning Microscopy (CLSM) was used to study surface topography previous and subsequent to the TPD measurements. The Keyence VK-X210 microscope with VK-X200K controller has a total magnification up to 24 000 \times . This consists of up to 150 \times objective lense magnification (Mo), up to 8 \times optical zoom and digital magnification. A laser with a wavelength of 408 nm is used for the illumination. For all images shown here, objectives with Mo = 10 \times (N.A. = 0.3) and Mo = 150 \times (N.A. = 0.95) were used. The images are overlaid with widefield microscopic and laser intensity measurements.

3 Results

3.1 Reference mass spectra of the pure electrolytes

The investigations on the temperature behavior of the polyelectrolyte coated NaBD₄ samples are preceded by gaining

reference mass spectra of the pure electrolytes, which could not be found in the literature. The number of possible fragments desorbing from the polyelectrolyte films is far too big to monitor all of them. Thus, the most intense peaks were monitored as extracted from the reference mass spectra. On the other hand, all possible deprotonized fragments as well as typical atmospheric adsorbates were monitored for the NaBD₄ samples.

The eligible fragments of PABA and PEI were measured by electron impact mass spectrometry at 20 eV as shown in Fig. 1 and Fig. 2, respectively. A selection of the monitor masses used later on has been denoted by arrows and the corresponding mass values within the spectra. Further measurements were made with electron impact ionization at 70 eV as well as chemical ionization at 4 hPa methane and 70 eV. Basing on these results, the monitor masses have been chosen within the 300 u range of the QMS system. The chosen peaks had to fulfil the criteria to be prominently visible in all the spectra performed at the three different ionization methods (electron impact ionization at 20 eV, electron impact ionization at 70 eV and chemical ionization using 4 hPa methane at 70 eV).

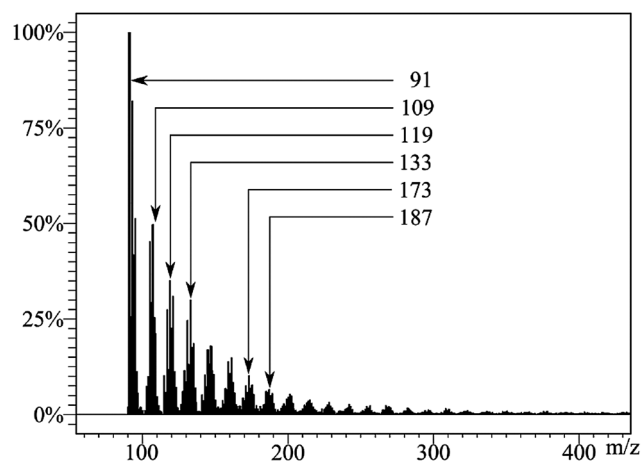


Fig. 1 Mass spectrum of the electrolyte PABA.

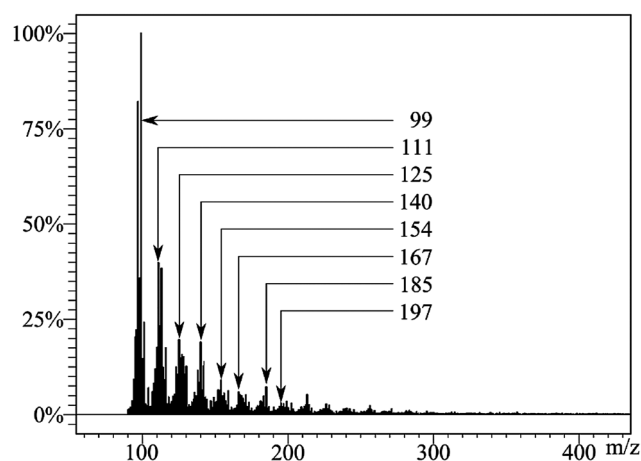


Fig. 2 Mass spectrum of the electrolyte PEI.

3.2 Temperature behavior of pure NaBD₄

Fig. 3 shows the desorption rates of the monitored masses from NaBD₄ as a function of the temperature. The heating current was increased by 0.2 A every 30 min, thus allowing the samples to achieve a dynamic equilibrium temperature and desorption rate. This has been done with respect to the application, which would most probably take place at a constant temperature. The measurement of the partial pressures took place during the whole time span, thus allowing to identify even small desorption peaks. The most prominent features are visible for H₂O (dark blue lines and left-pointing triangles) with maxima around 90 °C and 130 °C. This course is well reproduced by the desorption rates of OH (light blue lines and diamonds) and atomic oxygen (light green lines and downward-pointing triangles) as the fragments of water. Thus, no other significant source of hydroxy-groups or oxygen can be present. The desorption rate of carbon monoxide (purple lines and right-pointing triangles) shows one small maximum around 100 °C, which can be attributed to the carbon oxides from air that were chemisorbed within the sample's water adlayer. The desorption rates of atomic deuterium (red lines and circles) and molecular deuterium (dark green lines and upward-pointing triangles) behave similarly with a small maximum around 110 °C and a much larger maximum around 175 °C. No contribution of sodium- or boron-containing compounds (not shown within the figure) were found until 225 °C, while the decomposition of the sample starts above this temperature.

3.3 Influence of PABA on the temperature behavior of NaBD₄

Fig. 4 displays the desorption rates of selected items of the monitored masses over the sample's temperature for a PABA film prepared on a molybdenum sample (top frame) and the

desorption rates of the PABA coated NaBD₄ sample as a function of temperature (bottom frame).

The desorption rate of atomic hydrogen from PABA on molybdenum (black lines and squares) has a prominent peak around 90 °C, which is not the case for molecular hydrogen (red lines and circles). For carbon monoxide (purple lines and right-pointing triangles), a first small peak can be found around 105 °C. The desorption rates of water (blue lines and left-pointing triangles) start to increase at 90 °C and reach a maximum around 150 °C. No characteristic desorption features seem to be visible for atomic oxygen (green lines and downward-

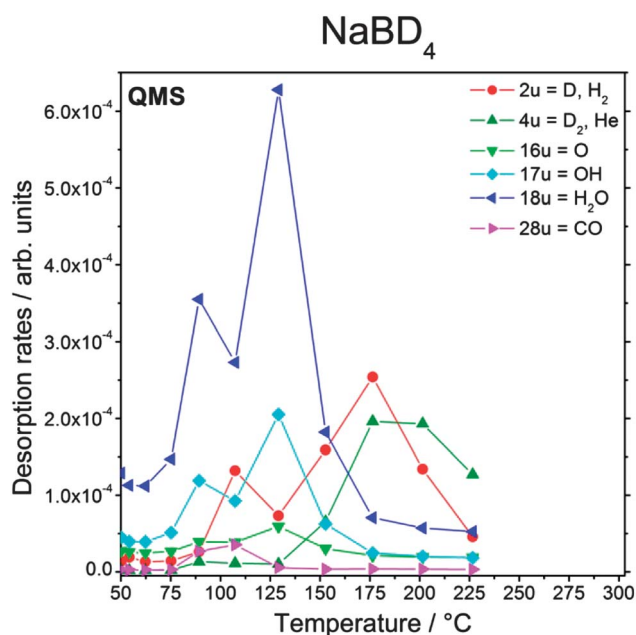


Fig. 3 Temperature-programmed desorption rates from NaBD₄ for selected fragments and adsorbates.

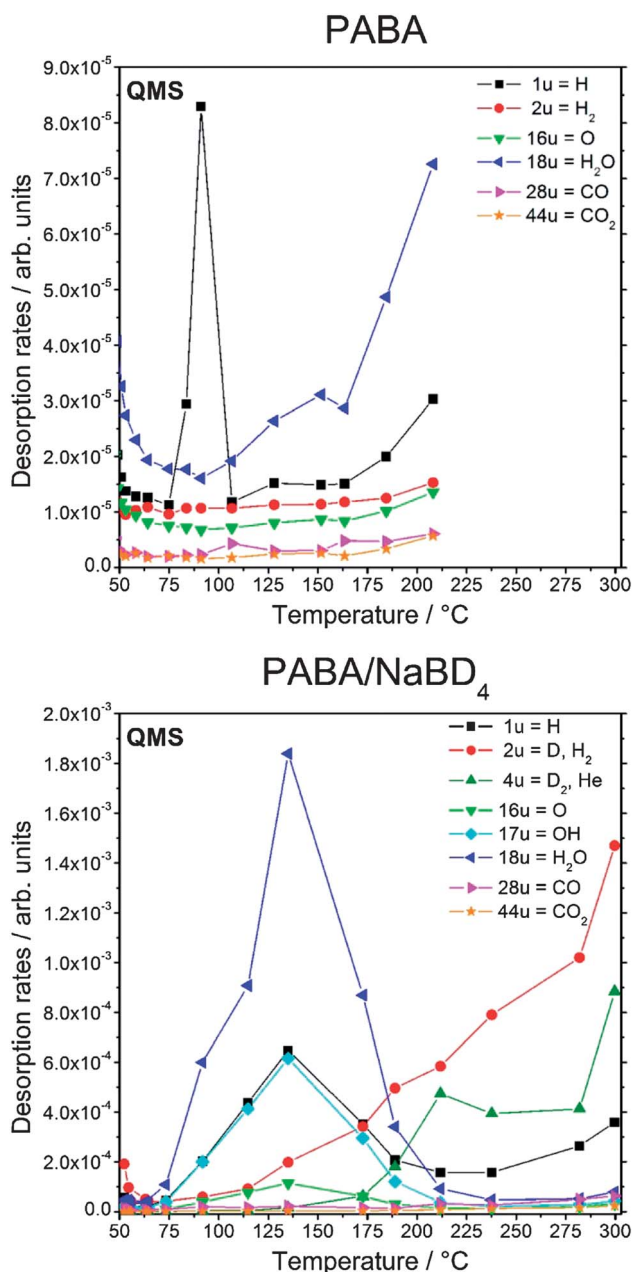


Fig. 4 Temperature-programmed desorption rates from PABA-covered molybdenum for selected fragments and adsorbates (top frame) as well as from PABA-covered NaBD₄ for selected fragments and adsorbates (bottom frame).

pointing triangles), carbon dioxide (orange lines and stars) and molecular hydrogen until 160 °C, where all displayed monitor masses slowly start to increase. At 210 °C, the desorption of whole fragments of PABA begins (not shown) as indicated by the desorption rates of the corresponding monitor masses.

The water desorption from PABA coated NaBD₄ (dark blue lines and left-pointing triangles) shows a maximum at 135 °C and a shoulder around 90 °C, which is very similar to the findings for the pure NaBD₄ even though the features seem to be slightly broadened for the PABA coated sample. The desorption of hydroxy groups (light blue lines and diamonds), atomic oxygen (light green lines and downward-pointing triangles) and atomic hydrogen (black lines and squares) follow the development of the water desorption, while an increasing hydrogen desorption starting from 190 °C indicates a surplus source for atomic hydrogen. No significant desorption features are visible for carbon monoxide (purple lines and left-pointing triangles) as well as carbon dioxide (orange lines and stars). The desorption of molecular deuterium (olive-green lines and upward-pointing triangles) begins around 120 °C, it shows a maximum at about 210 °C and later on strongly increases starting from 285 °C. The desorption rate for monitor mass 2 u includes the desorption of molecular hydrogen as well as atomic deuterium. Thus, the first raise between 70 °C and 130 °C is most probably hydrogen from water fracturing following the H₂O desorption, taking into account intensity ratios of 1 : 0.35 for water and mass 1 u and 1 : 0.11 for water and mass 2 u, while cracking usually occurs at ratios of 1 : 0.40 and 1 : 0.26, respectively, as estimated from water reference measurements. Above 130 °C, the measured desorption rate for monitor mass 2 u continuously increases, which is most probably solely due to deuterium release from the NaBD₄, since it is not accompanied by an increase of desorbed water. The desorption of fragments from the NaBD₄ (not shown) slowly starts above 280 °C.

Fig. 5 shows CLSM pictures of PABA coated NaBD₄ before (left) and after (right) the thermal desorption experiments. Top pictures have a magnification of Mo = 10×, *i.e.* showing a field

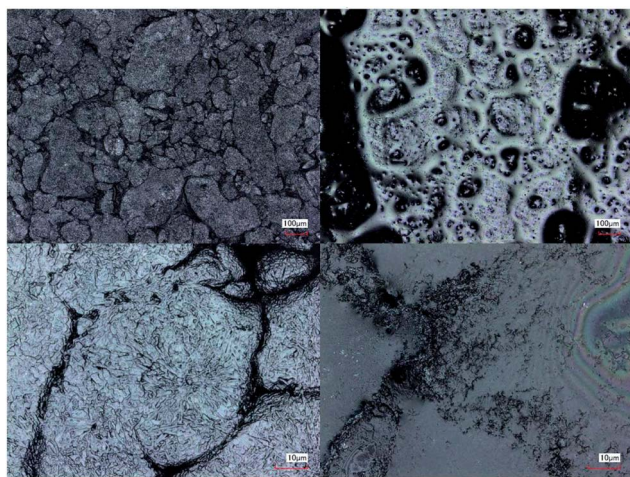


Fig. 5 CLSM images of PABA-covered NaBD₄ before (left) and after (right) the temperature treatment with image sizes of 1408 µm × 1056 µm for the top images and 95 µm × 71 µm for the bottom images.

of view (FOV) of 1408 µm × 1056 µm. The bottom ones using Mo = 150× show a FOV of 95 µm × 71 µm. Before the temperature treatment, one can see the compressed micrometer sized NaBD₄ powder. Afterwards the interspaces between these particles are filled up, while some larger holes have been formed.

3.4 Influence of PEI on the temperature behavior of NaBD₄

Fig. 6 shows the desorption rates of the monitored masses from a PEI film prepared on a molybdenum sample (top frame) and a PEI coated NaBD₄ sample (bottom frame).

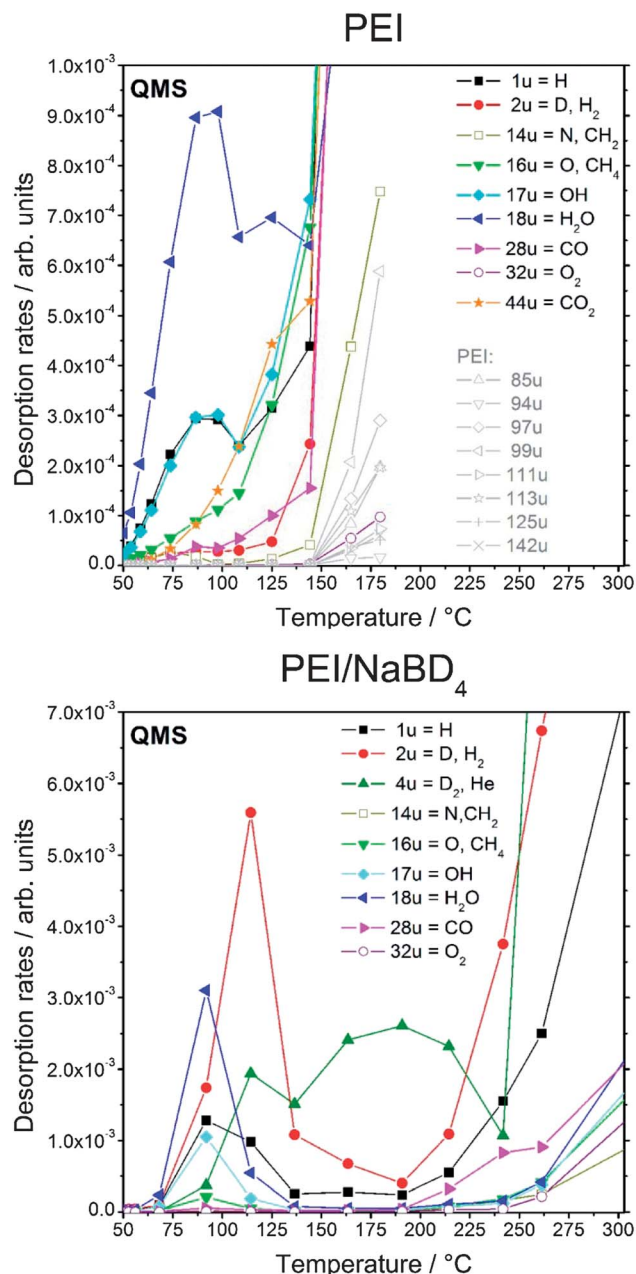


Fig. 6 Temperature-programmed desorption rates from PEI-covered molybdenum for selected fragments and adsorbates (top frame) as well as from PEI-covered NaBD₄ for selected fragments and adsorbates (bottom frame).

For the PEI film on molybdenum, a desorption maximum is found for water (dark blue lines and left-pointing triangles) as well as hydroxy groups (light blue lines and diamonds) and hydrogen (black lines and squares) as the typical fragments of water. A slight increase with raising temperatures is visible for atomic oxygen (light green lines and downward-pointing triangles), carbon monoxide (purple lines and right-pointing triangles) and carbon dioxide (orange lines and stars). At temperatures higher than about 145 °C, the strong increase of all desorption rates including the PEI monitor masses (all gray lines and icons) indicate the complete decomposition of the PEI.

From PEI coated NaBD₄, the desorption maximum of water (dark blue lines and left-pointing triangles) as well as hydroxy groups (light blue lines and diamonds) and atomic hydrogen (black lines and squares) around 90 °C is succeeded by a significant desorption maximum of atomic deuterium (red lines and circles) and molecular deuterium (olive-green lines and upward-pointing triangles). A desorption minimum of atomic deuterium in between 135 °C and 240 °C is accompanied by a broad desorption maximum of molecular deuterium. All desorption rates including the PEI monitor masses (not shown) significantly increase above 240 °C, thus indicating a beginning decomposition of the PEI.

Fig. 7 shows light microscopy (top right) and CLSM (others) pictures of PEI coated NaBD₄ before (left) and after (right) desorption. Top pictures have a magnification of Mo = 10× (FOV 1408 μm × 1056 μm). The bottom ones have Mo = 150×, *i.e.* a range of 95 μm × 71 μm. Compressed micrometer sized NaBD₄ particles are visible before desorption similar to Fig. 5. Afterwards the microparticles interspaces are filled as indicated by the top right picture. There is also a translucent droplet on the surface of the temperature-treated, PEI coated NaBD₄ sample which might be due to a segregation of the PEI.

3.5 Comparison of both electrolytes

The influence of the electrolytes on the temperature behavior includes two main effects, the enhancement of deuterium

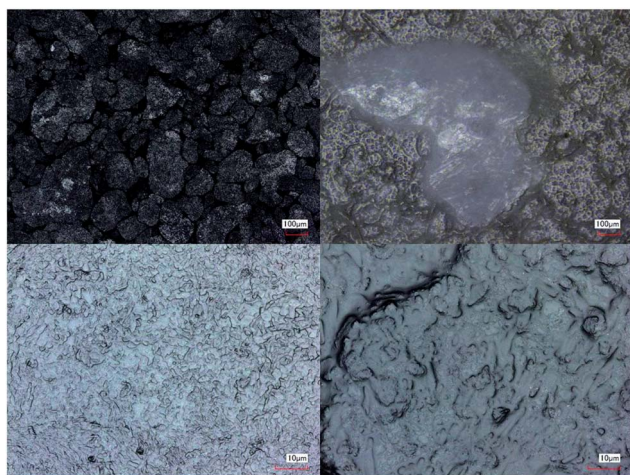


Fig. 7 CLSM images of PEI-covered NaBD₄ before (left) and after (right) the temperature treatment with image sizes of 1408 μm × 1056 μm for the top images and 95 μm × 71 μm for the bottom images.

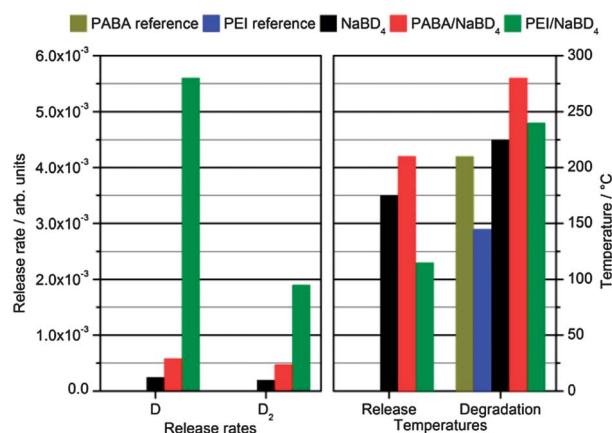


Fig. 8 Evaluation of the maximum release rates of atomic and molecular deuterium as well as the optimum release and the degradation temperatures with image sizes of 1408 μm × 1056 μm for the top images and 95 μm × 71 μm for the bottom images.

release and the stabilization of the NaBD₄ substrate. For easy comparison, the maximum release rates of atomic and molecular deuterium, the corresponding optimum release temperatures and the degradation temperatures have been displayed for all of the samples in Fig. 8.

The release of atomic and molecular deuterium increases by 2.3 and 2.4 for the PABA coated NaBD₄ and by 22.4 and 9.7 for the PEI coated NaBD₄ in comparison to the uncoated NaBD₄ sample, respectively. Thus, the enhancement of the deuterium release is more sufficient by one order of magnitude for the PEI coating rather than the PABA coating, even though both electrolytes show an enhancing effect.

The optimum release temperature of about 175 °C for the uncoated NaBD₄ sample increases up to 210 °C for the PABA coated NaBD₄ sample, while it decreases down to 115 °C for the PEI coated NaBD₄ sample. The degradation temperature of about 225 °C for the uncoated NaBD₄ samples increases up to 280 °C and 240 °C for the PABA coated NaBD₄ sample and the PEI coated NaBD₄ sample, respectively, even though the electrolyte references indicated degradation temperatures of 210 °C and 145 °C for the pure PABA and the pure PEI samples. Therefore, the optimum release temperature is 50 °C below the degradation temperature for the pure NaBD₄ sample, 70 °C for the PABA coated NaBD₄ sample and 125 °C for the PEI coated NaBD₄ sample.

4 Conclusions

The polyelectrolytes PABA and PEI have both been found to enhance the deuterium release rate and temperature stability of NaBD₄ powder samples. However, the deuterium release enhancement was about one order of magnitude more efficient for the PEI coating than for the PABA coating. Furthermore, the PEI coating significantly lowered the optimum release temperature, while it got slightly risen by the PABA coating. Therefore, the PEI coating has been found to be far superior to the PABA coating with respect to the application, even though the PABA

coating still represents an improvement over the uncoated NaBD₄ sample.

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