Accurate measurement of hydrogen concentration in transition metal hydrides utilizing electronic excitations by MeV ions

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ARTICLE INFO
Handling Editor: Umit Demirci

Keywords:
Hydrogen detection
Ion beam analysis
Transition metal hydrides
Hydrogen-rich materials
Electronic excitations
Hydrogen storage

ABSTRACT

This study focuses on enhancing the accuracy of hydrogen content verification in hydrogen-rich ultrathin materials relevant for sustainable energy applications. Ion beams are used for distinctive real-space detection leveraging elastic and inelastic interactions with hydrogen atoms. However, the lack of experimental reference data on electronic interactions poses a challenge to the accuracy of analytical techniques. We investigate the effect of absorbed hydrogen on the electronic energy deposition of N-ions in amorphous transition metal compounds, specifically V and Zr, covering concentrations >1H/M. Employing resonant nuclear reactions and Rutherford backscattering, the energy loss is found to increase considerably with hydrogen content, in line with Bragg’s additivity. The electronic energy loss cross section for N-ions at 6.5 MeV measured (64.55±3.38) eV cm²/10¹⁵ atoms. Results are compared to semi-empirical and theoretical models. The findings improve hydrogen profiling accuracy using N-nuclear reaction analysis and enable unprecedented methods for hydrogen quantification by other, commonly available ion beams.

1. Introduction

Hydrogen-rich hydrides with transition metals offer reversible hydrogen storage solutions [1–6] and are important for fuel cell applications [7–10], battery electrodes [11,12], and superconductors [13–15]. Their exceptional thermodynamic characteristics support the storage of thermal energy, hydrogen compression, and heating and cooling systems [16–20]. Due to their dynamic optical and electrical properties, they enable sensors, smart mirrors, and windows [21–25]. The interaction of energetic ions with hydrogen in these materials and accurate knowledge of ion energy deposition is critical for various ion beam analysis techniques, including sample depth profiling [26], material modification [27,28], and beam-patterning for nanotechnology [29]. Energetic ¹⁵N-ion beams are selectively sensitive to hydrogen with ~10¹⁸ atoms/cm³ allowing direct concentration measurements via nuclear reaction analysis (NRA) [30] in materials. The concept of depth-resolved NRA is based on the loss of kinetic energy of ¹⁵N-ions when traveling through compounds. Hence, understanding and predicting the influence of hydrogen energy loss is essential for hydrogen-containing materials and applications, given ongoing efforts to develop new high-hydrogen-content materials and tailoring properties towards applications. Further, implications extend beyond metal hydrides, encompassing fundamental and diverse aspects of materials science [31–34], including applications in nuclear energy, aerospace, and medical technology. Heavy ion beams like nitrogen are especially effective in cancer therapy [35,36], cosmic ray shielding tests [37], and studies of materials for fusion energy [38]. The continuous loss of kinetic energy in energetic ions passing through matter, known as stopping power S = dE/dx, primarily arises from interactions with target atom electrons through elastic binary collisions rather than target nuclei. The kinetic energy transfer to the electronic subsystem includes a number of mechanisms that depend in a non-trivial way on the target, the projectile, its velocity, and charge. Target atoms can be excited and ionized by the projectiles, which can in return undergo excitation and change charge states by capture and loss of electrons. Programs like CasP [39] and PASS [40] generate predictions based on theoretical approximations, however, no universal model covers all energies and ion-target combinations. Verification experiments are required and the results are collected in a database by the IAEA [41]. Unfortunately, data is lacking for many ion-target combinations or the available data sets deviate beyond their uncertainties. Semi-empirical tools like SRIM [42] use available datasets to predict energy loss for any ion-target combination and energies. A recent neural network code, ESPNN [43], predicts electronic stopping power using the

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https://doi.org/10.1016/j.ijhydene.2024.01.032
Received 25 October 2023; Received in revised form 22 December 2023; Accepted 3 January 2024
Available online 12 January 2024
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filtered IAEA database. Still, challenges persist for multi-element targets or changes in aggregation states. Bragg’s rule estimates compound stopping powers as weighted mean of elemental standards [44] but in the absence of chemical state effects. All too often deviations from Bragg’s additivity occur, particularly in compounds of light elements due to strong hybridization and valence structure changes [45–48]. Furthermore, target aggregation state alterations can induce various simultaneous processes that influence the energy transfer. For example, screening effects by metal conduction electrons on light ion projectiles can decrease the electronic stopping power compared to the gas phase [49,50]. Contrary, for very heavy ions the high density of solid targets influences the charge exchange processes and increases the effective charge state of ions, which correlates to higher stopping relative to the gas phase [51]. Energy loss by hydrogen absorbed in metals might be subject to both chemical and physical state effects. S. Yamaguchi et al. observed that He-ion stopping power was lower for implanted hydrogen in silicon compared to hydrogen in Al-3.5 % Li, where it agglomerates in blisters and is possibly gaseous [52], suggesting a physical state effect. Hydrogen absorbed in transition metals, described as lattice gas [53], induces modifications to their electronic structure, especially in group III metals where metal-insulator transitions may occur [25]. These changes are commonly induced by hybridization between the hydrogen 1s- and metal d-electrons [54]. Therefore, hydrogen’s stopping power for heavier ions, i.e., nitrogen, having several charge states at intermediate energies in targets of transition metal compounds, represents a comprehensive precedence, that is studied in this work.

The absence of benchmark data impedes the range and accuracy of analysis methods by means of ion beams and also hampers the advancement of theoretical models and predictive methods. By addressing these gaps in knowledge, our research contributes to paving the way for improved analytical methods and enabling new indirect detection methods accessible at a larger number of laboratories.

2. Experimental methodology

To study hydrogen’s impact on 15N-ion energy deposition, the V$_x$Zr$_{1-x}$ metallic glass system was selected as a model system due to its high affinity for hydrogen and good mass contrast. The V$_x$Zr$_{1-x}$ alloys have nominal compositions of $x$ = 30, 50, 66, 80 while the variable hydrogen content is not included in the notation throughout this work. Thin films of V$_x$Zr$_{1-x}$ with nominal thicknesses of 400 Å and 500 Å were grown by direct current magnetron sputtering on amorphous SiO$_2$ substrates and confirmed as amorphous through grazing incidence XRD measurements following the procedure in Ref. [55]. The samples are capped with 6 nm Al$_2$O$_3$ to prevent oxidation and hydrogen loss during ion beam analysis [56] and 6 nm Pd to catalyze hydrogen absorption during loading.

Samples are hydrogenated in a temperature-controlled ultra-high vacuum chamber, heated to 150 °C, and exposed to pressures up to 500 Torr of purified hydrogen from a metal hydride. After several hours, the chamber is gradually evacuated and cooled to room temperature. The compounds are expected to remain metallic after hydrogen absorption [55].

Ion beam experiments were done at the 5 MV 15 SDH-2 tandem accelerator, Uppsala University, Sweden [57]. The composition and areal density of the layers were determined using Rutherford backscattering spectrometry (RBS) with 2 MeV primary 4He-ions. RBS spectra were acquired at incident angles of 5° and 60° to enhance depth resolution. Backscattered ions were detected by a semiconductor detector with a 15 keV FWHM resolution at a 170° scattering angle. Calibration of the energy abscissa was achieved by measuring surface edges on several elemental bulk reference samples. Experimental spectra were analyzed using SIMNRA simulation software [58], utilizing the SRIM-2013 stopping power dataset as preliminary input. Manual iterations were performed to fit spectrum heights and integrals. The accuracy of resulting film areal densities relies on the accuracy of the SiO$_2$ substrate’s stopping power input, as it influences the substrate spectrum’s height fitted by the number of impinging particles [26]. Some RBS measurements were charge-normalized by alternating measurements with a thick Cu foil reference of 99.999+1% purity over 25 repetitions, hence ensuring equivalent exposure for both samples. The analysis method using Cu as a reference is detailed in Ref. [59]. SRIM-2013’s stopping power predictions for 4He-ions on Cu were found to be accurate over a wide energy range. The number of impinging ions on the detector was determined by integrating the backscattering yield near the Cu leading edge, unaffected by surface contaminants, with a relative standard uncertainty below 0.4 %. Subsequently, the RBS spectra of the thin films on SiO$_2$ were simulated for this number of projectiles. To match the simulation and experiment, stopping powers were manually adjusted through a multiplicative correction factor applied to default predictions, ensuring convergence of the integral count. The universal screening potential was employed for all simulations, with scattering cross-sections based on the Sigma-Calc model.

A measure of the hydrogen density $n_H$ in the films, which is complemented with the hydrogen stopping power in an uncorrelated experiment, is performed by NRA via the $^1$H($^{15}$N, $^4$He) reaction. The $^{15}$N-ion beam energy varies between 6.37 and 6.65 MeV, positioning the resonance energy $E_{r}$ = 6.385 MeV at varying depths in the target. Ion fluences were kept below 2 nA. The $\gamma$ (4.43 MeV) radiation resulting from the nuclear reaction is detected with a Bismuth Germa-nate scintillation crystal placed outside of the experimental chamber behind the sample [60]. Given the amorphous structure, no channeling effects are considered [61]. The reaction yield vs. incident projectile energy, denoted as $Y(E)$, serves as a relative measure of $n_H$ distribution. $Y(E)$ depends however on the number of impinging ions $N$, $\gamma$ detection efficiency $\epsilon$, and is convoluted with an effective Voigt-shaped instrumental resolution function. This function accounts for broadening effects of the resonant reaction energy range, besides the nuclear resonance width $\Gamma$, namely the energy distribution of the incident ion beam, Doppler-effects due to zero-point vibrations, and ion straggling in the target material [20]. Absolute $n_H$ values are determined from $Y(E)$ via numerical deconvolution. The procedure simplifies for a target of homogeneous hydrogen density, where $Y(E)$ remains constant at projectile energies well above $E_R$ and is therefore proportional to $n_H$ [26]:

$$Y(E > E_R) = \frac{\pi}{2} K N \epsilon n_H \frac{n_{ref}}{N}$$

where $\sigma$ is the nuclear resonance cross-section. $S$ depends on the ion energy $E$. However, the energy loss in surfaces and thin films is relatively small (<0.15 MeV), and therefore, the modification of $S$ is negligible.

The experimental setup is calibrated to its characteristic $\gamma$-detection sensitivity through a single reference measurement of $Y_{ref}$ and $n_{ref}$ on a sample with known bulk hydrogen density $n_{ref}$ and stopping power $S_{ref}$. The calibration covers all parameters in eq. (1) other than $N$, $n_{H}$, $S_{ref}$ and is performed on an H-implanted Si-standard of 18.5 % with systematical uncertainty 2–3% which is not included in the analysis procedure. In practice, $n_H$ is obtained by converting $Y(E)$ via:

$$n_H = \frac{Y_{ref} S_{ref} n_{ref} n_{H} \epsilon_{ref}}{Y(E) S n_{H} \epsilon_{ref}}$$

The perceived depth ($d = \Delta E/\Delta S$) and $n_H$ scale with $S_{H}$, the stopping power of the investigated material. To first approximation the stopping cross section of the compound $c$, the energy loss normalized by the atomic density of the material $S/n$, can be estimated by the Bragg rule [4*] as a linear combination of its constituent elements’ i stopping cross section $c_i$:

$$c = \sum c_i c_i = c_H c_I + c_C c_E + c_I c_H$$

where $c_i$ are the atomic fractions.

A challenge in extracting the stopping cross section of hydrogen $c_H$ in the V/Zr compound is that $c_i$ needed to calculate $n_H$, does itself depend on the hydrogen content $c_I$. Conventional hydrogen depth profiling is
Based on solving equations (2) and (3) by an iterative approach, using tabulated values for individual $e_i$. Several iterations yield consistent values of $n_H$ and $S_{MH}$ [30]. In this study, however, the energy loss in hydrogenated $V_xZr_{1-x}$ films is determined independent of the hydrogen content, by integrating $^{15}$N-RBS into the analysis of $^{15}$N-NRA yield curves.

Due to its low mass, hydrogen is not directly detectable using $^{15}$N-RBS. Instead, we rely on its influence on the stopping power in the $V_xZr_{1-x}$ layer. The hydrogen stopping cross-section is inferred from the backscattering yield of $V$ and $Zr$ atoms, indicated by the height of the backscattering signals and the difference in kinetic energy of ion projectiles backscattered from the top and bottom of a thin film $\Delta E$ [16]. Backscattered $^{15}$N-ions are detected at a 160° scattering angle using a solid-state detector in the chamber [60]. To extract $e_i$, SIMNRA simulations [58] are fitted to the recorded spectra incorporating target information from the $^{4}$He-RBS analysis. Stopping powers for non-absorbing layers follow the latest SRIM-2013 version, while those in the hydrogenated $V_xZr_{1-x}$ layers remain variable. Manual iterations of the simulation are conducted to achieve agreement of height and width $\Delta E$ between experimental and simulated spectra. The detector energy calibration is pre-established through reference measurements, and the projectile number is fitted to the $P_d$ peak. The sole adjustable parameter in the calculations is the multiplicative correction factor for energy loss, which can be determined within an uncertainty of 1.75 % on average. The choice of screening potential models, Anderson or Universal, has a negligible impact on the integral count, so the Universal potential is adopted.

Implementing measured $e$ values, the NRA-yield can be scaled to $n_H$ after converting to $S_{MH}$ with the layer’s nominal thickness. Hydrogen-induced lattice expansion is not considered since volume changes cancel out during the analysis, due to normalization by atomic densities, and since the RBS-yield is only sensitive to the layer areal atomic density and not the actual thickness. Finally, equations (2) and (3) are solved to extract $e_i$ in the transition metal compounds:

$$e_i = \frac{S_{MH} - S_M}{n_i} = \frac{N}{F_i}\left(\frac{S_{MH} - S_M}{S_{MH}}\right) \cdot K$$

(4)

where calibration parameters for NRA are summarized by $K = Y_{ref}/N_{ref}$, $S_{ref}$ and $S_M$ is the stopping power of the pristine $V_xZr_{1-x}$ layer. The expression depends solely on parameters measured independently in this study. An advantage of this analysis is that uncertainties in nominal thickness or volume changes equally impact both sides of the equation, canceling each other out.

3. Results and discussion

Fig. 1 presents the RBS spectra from $V_xZr_{100-x}$ samples obtained with 2 MeV $^4$He-ions at 60° incident angle and corresponding simulation by SIMNRA [58]. The analysis of charge normalized spectra reveals an averaged correction factor of 0.965 for the energy loss in SiO$_2$ relative to the prediction by SRIM-2013, which is consistent with other experiments [62]. This correction is applied to all simulations of $^4$He-ions in SiO$_2$ in this work. Additional corrections to the transition metal stopping cross sections are required to accurately reproduce the experimental spectra. For $Zr$, an average correction factor of 0.841 is needed when using experimental values for $V$ [59]. This correction is reasonable considering experiments on neighboring elements [63]. Hydrogen contaminants in the films, discussed in the following chapter, are estimated to contribute by <1 %. The film composition, denoted as $x$, remains homogeneous and within 1 at. % of the nominal composition. Target models, containing areal densities and elemental compositions for each layer, were established based on experimental spectra obtained at incident angles of 5° and 60°.

Fig. 2 displays exemplary NRA yield curves for hydrogenated $V_xZr_{1-x}$ samples. The $\gamma$-yield is normalized by the relative cumulated ion fluence, without accounting for energy loss or detection efficiency. The flat plateaus within the 6.48–6.55 MeV energy range indicate homogeneous hydrogen distribution in $V_xZr_{1-x}$ layers. Differences in the $\gamma$-yield plateau widths are not necessarily due to variations in film thickness but relate to the energy loss since the conversion from $^{15}$N-ion energy inversely scales with $S_{MH}$. While plateau width could serve as a measure of total energy loss in hydrogenated films, it is sensitive to interface effects and becomes challenging for samples with low hydrogen content. The yield curves are averaged over the plateau for $n_H$ analysis.

Fig. 3 shows subsequently acquired backscattering spectra of 6.6 MeV $^{15}$N-ions for a $V_xZr_{1-x}$ layer ($x = 66$) in its pristine and hydrogen-loaded state. Note that the pristine samples contained trace amounts of hydrogen, as revealed by NRA. SIMNRA simulations are fitted to the experimental spectra, adjusting the multiplicative correction factor for the stopping power of $V_xZr_{1-x}$. The presence of sharp edges on the lower energy side of the plateaus indicates that plural and multiple scattering events have minor effects, rendering the single scattering approximation in the simulation an accurate representation of the experimental spectra [64]. Differences between the hydrogen-loaded and pristine samples are evident. Hydrogenated $V_xZr_{1-x}$ layers exhibit a wider energy range among backscattered ions, requiring increased energy loss in the simulations corresponding to an increase in total stopping power as absorbed hydrogen atoms contribute their electrons to the compound. Electronic stopping dominates in our case, with the nuclear contribution being less
Fig. 3. RBS spectra for 6.6 MeV primary $^{15}$N-ions backscattered from (a) pristine and (b) hydrogen-loaded $V_xZr_{1-x}$ compound for incident angle of 60° and detection angle of 160° (black symbols and line). Simulations using SIMNRA [58] are represented by the thick solid lines. The energy loss in the layer is fitted to the heights, the integral count within the indicated energy range, and the widths $\Delta E$ of the backscattering plateaus, which corresponds to the difference in kinetic energies of ions scattered from atoms at the top and bottom of the $V_xZr_{1-x}$ compound.

Fig. 4 summarizes the compound stopping powers $S_{\text{MH}}$ determined from simulated total energy loss in $V_xZr_{1-x}$ layers with varying hydrogen content, normalized to film thickness. The values $n_H$ are extracted from NRA yield curves, scaled by individual $S_{\text{MH}}$ values. $S_{\text{MH}}$ increases linearly with $n_H$ for each material composition $x$. As the compounds of V and Zr under investigation always contained hydrogen, the electronic stopping cross sections of pure metals $\epsilon_V$ and $\epsilon_Zr$ cannot be directly determined. Hence, extrapolation is applied to datasets spanning a wide $n_H$ range, using linear regression with direct weighting to obtain compound $S_{\text{MH}}$ values. Conversion to electronic stopping cross sections [eV cm$^2$/10$^{15}$ atoms] is accomplished with areal densities and compound composition $x$. In the inset of Fig. 4, resulting compound electronic stopping cross sections are plotted against $x$. Following Bragg’s additivity rule, a weighted linear regression is performed and extrapolated to $x=0$ and $x=1$. This yields values of (426.6 ± 12.4) and (521.6 ± 12.74) eV cm$^2$/10$^{15}$ atoms for pure V and Zr, respectively, deviating by correction factors of 1.018 and 0.854 from SRIM-2013. $S_{\text{MH}}$ values are recalculated for each compound $x$.

Fig. 5 displays the change in stopping power $\Delta S = S_{\text{MH}} \cdot S_{\text{H}}$ for the $V_xZr_{1-x}$ compounds as $n_H$ varies. The datasets for different compounds $x$ coincide within their uncertainty, showing a linear increase with $n_H$. Using eq. (4), the electronic stopping cross section per absorbed hydrogen atom $\epsilon_H$ is calculated for each measurement and plotted against $n_H$ in Fig. 5 (bottom). Notably, $\epsilon_H$ is itself not dependent on $n_H$, and a weighted arithmetic mean of values exceeding $4 \times 10^{22}$ atoms/cm$^2$ yields (64.55 ± 3.38) eV cm$^2$/10$^{15}$ atoms. As the energy loss follows a simple additivity rule for the pure metals and with $\epsilon_H$, the transition metal hydrogen compound is overall perceived as a mixture.

In Fig. 6 the result is compared with literature data and calculated values of $\epsilon_H$ over an extended energy range. Literature data from Refs. [65,66], sourced from the IAEA database, pertains to measurements in H$_2$ gas. Due to significant differences in projectile energy ranges, a direct comparison to evaluate chemical or physical state effects is not feasible. A table in Ref. [26] presents calculated stopping power values for $^{15}$N at 6.385 MeV in all elemental targets, suggesting notably smaller stopping power than our experimental findings. Semi-empirical simulations using SRIM-2013 closely approximate our measured value. However, density and gas corrections within SRIM-2013 predict higher losses around and below the Bragg peak, inconsistent with experiments by Ref. [66]. An earlier study involving heavier ions $8<Z<92$ in H$_2$ gas found SRIM considerably underestimating stopping power relative to experimental values [67]. Simulations employing the neural network code ESPNN yield values significantly lower than experimental results. With CasP6.0 [39], $\epsilon$ is calculated from the H-1s electrons, scanning over different
projectile charge states using the unitary convolution approximation (UCA), both with and without the free-electron-gas approximation model for transport cross section (TCS). Negligible contributions from energy loss due to projectile ionization, excitation, and electron capture are observed in this model. These predictions are reasonably close to the measured value at the investigated projectile energy. Casp6.0’s gas target correction predicts much lower energy loss, even below the experimental value [66]. This correction model attributes the lower energy loss to the assumption of a decreased mean projectile charge state in gas targets with lower density, consistent with observations for heavy ions in Ref. [51]. This effect stands in contrast to SRIM and [49], which predict the opposite impact of a change in physical state on electronic energy loss, including target-induced projectile ionization, excitation, and capture, is 377.9 eV cm$^2$/10$^5$ atoms. These findings have implications for hydrogen detection by the use of ion beams especially for hydrogen-rich transition metals where hydrogen’s energy loss contribution is significant. The compound stopping power, crucial for scaling resonant nuclear reaction yields with $^{15}$N-NRA to absolute hydrogen concentration, can be determined accurately on the basis of the results. The study validates the practice of using the simple additivity rule, indicating its applicability to a wide class of materials. Furthermore, they pave the way for novel methods to gauge hydrogen concentration indirectly, such as analyzing Rutherford backscattering spectra employing various ion species without relying on nuclear reactions. This advancement enables quantitative assessment of hydrogen concentrations with an estimated sensitivity to $>10^{22}$ atoms/cm$^2$ in solids across a wider range of facilities.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Acknowledgments**

The authors gratefully acknowledge financial support of the Tandem accelerator infrastructure by VR-RFI (contract #2017-00646_9) as well as the Swedish Foundation for Strategic Research (SSF) under contract RIF14-0053.

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