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ABSTRACT
The use of hydrogen atoms for magneto-ionic applications has only been explored recently. Benefits of hydrogen compared to other ionic species for tuning magnetism are high switching speed and large changes in magnetic moment. Here, we test the influence of hydrogen intercalation on magnetism in nanoporous Pd$_{1-x}$Co$_x$, with Co being located in superparamagnetic clusters, building upon a previously suggested material system. Tailoring the Co concentration and distribution allows the magnitude of the magneto-electric effect to be influenced as well as to gain a deeper understanding of the interaction of hydrogen with magnetic clusters. In situ magnetization measurements are conducted to directly observe the variation in magnetic moment upon hydrogen-charging in nanoporous Pd$_{1-x}$Co$_x$. Temperature-dependent magnetization curves show that interstitial hydrogen atoms lead to an increase in magnetic anisotropy energy, a coupling of individual Co-rich clusters, and the concomitant blocking of their magnetic moments. The large obtained magnetic switching effects upon hydrogen-charging at room temperature ($\alpha_{C,V} > 400$ Oe V$^{-1}$; $\Delta M = 1.5$ emu g$^{-1}$) open up new possibilities to use magneto-ionic effects for real-life applications in magnetic devices.

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I. INTRODUCTION
Hydrogen, as the smallest atom in the Periodic Table, is able to form interstitial compounds with several metals and alloys. They are not only attractive as a safe method for hydrogen storage but can also be used to alter electrical, optical, or magnetic properties of the host materials. In the simplest scenario, a hydrogen atom on an interstitial site donates its electron into the bands of the host material, raising the Fermi energy and changing the density of states at the Fermi level. One of the oldest examples for metal–hydrogen interaction is the palladium–hydrogen system, which has been known since the mid-19th century. To date, the palladium–hydrogen system has remained topical for fundamental research in catalysis, hydrogen storage, and fuel cells.

Hydrogen-induced property changes have been mainly achieved from the gas phase, while more recently focus has been shifted toward the “ionic” approach based on electrochemical hydrogen-charging from an electrolyte. A rather young field of research built upon such electrochemical reactions is the controlled tuning of magnetic properties, termed magneto-ionics. Compared to the conventional magneto-electric materials, magneto-ionic approaches have a direct advantage in that the electric-field screening in metals can be overcome by the use of chemical reactions. As chemical reactions are typically limited by the available surface area, recent research in this field has directed special attention to geometries with high surface-to-volume ratios, such as thin films or nanostructured systems. Ion intercalation reactions can lead to even larger active interaction volumes of ions with magnetic materials, offering the possibility to change bulk-magnetic properties instead of surface-magnetic properties of magnetic materials. Alteration of magnetic properties has been observed upon electrochemical intercalation of various smaller ionic species, such as Li$^+$, Na$^+$, F$^-$, or H$^+$.19,34,35
Hydrogen ions or atoms are particularly promising for magneto-ionic devices, as they promise fast ion diffusion and thus rapid switching of magnetic properties. First studies to tune magnetic properties of nanoporous(np) Pd(Co) have been done by our group using electrochemical hydrogen charging into the bulk, followed by hydrogen sorption in micrometer-sized SmCo5, with both systems exhibiting giant changes in magnetic properties.

In our preceding publication, hydrogen-induced switching of superparamagnetism was demonstrated for the first time. In that work, npPd containing small superparamagnetic Co-rich clusters prepared via the dealloying synthesis route was charged with hydrogen from alkaline potassium hydroxide solution, which is a standard electrolyte for electrochemical hydrogen-charging. Unexpectedly, large changes in magnetic moment were observed, which could not be explained using the simple electronic band filling picture in Pd. Other potential factors, such as the reduction in Co oxides on the surface as well as a magneto-elastic coupling of superparamagnetic particles, were considered unlikely in our previous publication. We interpreted the strong changes using a novel magneto-ionic coupling mechanism shortly summarized as follows: (1) Co is located in superparamagnetic clusters in npPd(Co), which are weakly coupled via a RKKY (Ruderman–Kittel–Kasuya–Yoshida)-type exchange interaction mediated by conduction electrons of the Pd matrix. (2) Hydrogen intercalation in Pd affects its electronic band structure and the spatial period of the RKKY exchange, which causes a strong, net magnetic coupling of neighboring Co-rich clusters due to the pronounced first ferromagnetic maximum of the RKKY function. (3) Larger superparamagnetic units lead to a larger magnetic moment and a prolonged superparamagnetic relaxation time due to an increased stability against thermal fluctuations and an eventual transition to ferromagnetism.

Considering the importance of superparamagnetic Co-rich clusters for the switching mechanism, we expect a strong influence of cluster size and distribution on the magneto-ionic effect. By tailoring the overall Co content x in npPd1−xCo via galvanodynamically controlled dealloying in this work, we show that this also affects both superparamagnetic cluster size and distribution. Using in situ hydrogen-charging in a SQUID magnetometer, we demonstrate that the magneto-ionic response of npPdi−xCo increases in this way. Zero-field cooled temperature scans of magnetic susceptibility upon hydrogen charging evidence variations in the magnetic blocking temperature $T_B$. This allows additional insights into the magneto-ionic tuning mechanism and the interaction of hydrogen with superparamagnetic clusters.

II. EXPERIMENTAL

Homogeneous Co$_{75}$Pd$_{25}$ alloy samples (thickness $\approx270 \, \mu m$, $3 \times 4 \, mm^2$) were prepared by an arc melting, annealing, and rolling procedure (see Ref. 34 for details). For dealloying, the alloy pieces were attached to an Au wire (0.25 mm, Mateck, 99.9%), which also served as a contact for the hydrogen charging tests. Dealloying of Co$_{75}$Pd$_{25}$ was conducted using the galvanodynamically controlled dealloying (GCD) procedure. Thereby, a typical potential static dealloying curve, where current decays gradually with time, is discretized into four steps of constant current [see Fig. 2(a)]. The nominal Co dissolution charge $Q_{\text{tot}}$ calculated via Faraday’s law, was distributed based on the four steps as follows: 0.32 $Q_{\text{tot}}$ at $I = 2 \, mA$, 0.43 $Q_{\text{tot}}$ at $I = 1 \, mA$, 0.22 $Q_{\text{tot}}$ at $I = 0.5 \, mA$, and 0.03 $Q_{\text{tot}}$ at $I = 0.1 \, mA$. To gain control over the residual Co content in the dealloyed, nanoporous sample, the duration of the second etching step (1 mA) was lowered by a fixed time to retain a certain amount of Co corresponding to a certain residual Co charge.

\[
Q_x = \frac{m_{\text{Co,x}}}{m_{\text{Co,alloy}}} Q_{\text{tot}},
\]

where $m_{\text{Co,x}}$ is the Co mass remaining in the nanoporous sample and $m_{\text{Co,alloy}}$ is the Co mass in the starting alloy. The remaining Co mass, $m_{\text{Co,alloy}}$, is related to $x_{\text{Co,nom}}$ via

\[
x_{\text{Co,nom}} = \frac{m_{\text{Co,x}}}{m_{\text{Co,x}} + m_{\text{Pd}}},
\]

where $m_{\text{Pd}}$ is the Pd mass, which remains unchanged during dealloying.

The charge $Q_x$ is calculated using Eqs. (1) and (2) to obtain nominal, residual Co weight concentrations $x_{\text{Co,nom}}$ of 0%, 3%, 6%, 9%, 12%, and 15% in the nanoporous samples. The net charge flow in the experiment $Q$ is determined by deducting $Q_x$ from the nominal dissolution charge $Q_{\text{tot}}$. This procedure to prepare dealloyed samples of a defined residual Co content was realized using an electrochemical cell in a three-electrode configuration connected to a potentiostat (Metrohm Autolab, PGSTAT128N). A commercial Ag/AgCl (3 M KCl) electrode (Metrohm) served as a reference, while a coiled Pd wire (Chempur, 99.95%, Ø 0.25 mm) was used as a counter electrode for dealloying. The electrolyte solution was 0.1 mol/l H$_2$SO$_4$.

Electrochemical cells for in situ hydrogen-charging SQUID measurements followed the established cell setup developed in our group, which is sketched in Fig. 1. It consists of a three-electrode setup in a nuclear magnetic resonance (NMR) tube compartment. npPdi−xCo working electrodes were mounted in the lower part of the tube in proximity to an Au-wire, which served as a quasi-reference electrode. An additional Au-contacted npPd platelet was used as a counterelectrode in the upper part of the electrolyte compartment to avoid a contribution to the measured magnetic signal. Tubes were filled with an aqueous potassium hydroxide solution (1 mol/l) prepared from KOH pellets (Roth, $\geq95\%$, p.a.) and high-purity water (Roth, ROTIPURAN, p.a.). The cells were filled with an electrolyte up to 3 cm off the top, allowing room for electrolyte expansion during the in situ zero-field cooling/field cooling (ZFC/FC) experiments.

The in situ cyclic hydrogen-charging experiments were controlled using a potentiostat (Metrohm Autolab, PGSTAT204). The magnetic field was held constant at 5000 Oe, and the temperature was fixed to 300 K. Each sample underwent the same potential-controlled cycling procedure with a scan rate of 0.5 mV s$^{-1}$ in a voltage window of $-0.9$ to $-0.4$ V (vs Au), corresponding to the region of dominating hydrogen adsorption, absorption, and desorption reactions. A total of ten cycles was recorded, of which only the last five are depicted (Fig. 4), when the samples exhibited already a steady, reproducible current response.

For the measurement of ZFC/FC magnetization curves upon hydrogen-charging, samples were loaded with hydrogen at a constant potential of $U = -0.9 \, V$, which was held during the entire ZFC/FC measurement and already 1 h ahead for the sample
X-ray fluorescence spectra of npPd$_{1-x}$Co$_x$ were obtained using a Panalytical Epsilon 1 XRF analyzer equipped with a Ag anode. Intensities of the Co and Pd peaks were used for the calculation of composition in a standardless analysis approach. Peaks associated with elements originating from the sample holder (Mylar® foil) were excluded for elemental analysis. Slight deviations from actual composition might occur due to the limited size of the used nanoporous samples.

### III. SAMPLE PREPARATION—GALVANODYNAMICALLY CONTROLLED DEALLOYING

The GCD method offers the advantage of an independent control of residual element content with an unchanging porosity, which is distinct from free corrosion or potential-controlled dealloying methods. Experimentally, Co concentrations $x_{\text{Co,XRF}}$ obtained via the GCD procedure in npPd$_{1-x}$Co$_x$ were determined using XRF spectrometry, with the results given in Table I and plotted in Fig. 2(b) as a function of nominal Co content $x_{\text{Co,nom}}$. It should be noted that real Co concentrations are expected to be higher than nominally fixed values, as minor side reactions (e.g., Pd oxidation) are consuming parts of the total charge. Indeed, the concentration detected in the XRF, $x_{\text{Co,XRF}}$, is about 5 wt. % higher than the nominal Co content chosen for GCD $x_{\text{Co,nom}}$. Considering these experimental results in Fig. 2(b), we can clearly state that GCD is able to tailor the total Co concentration in npPd$_{1-x}$Co$_x$. The porosity in the GCD process is expected to remain almost unaltered, which was confirmed by evaluating electrochemical double layer currents for npPd$_{1-x}$Co$_x$, which indicate similar surface areas (not shown). As demonstrated by KMC simulations and TEM imaging in our previous works, the zero-field cooling (ZFC) curves for npPd$_{1-x}$Co$_x$ with different Co contents in Fig. 3 (black solid lines) allow an estimate of the size and the size-distribution of the Co-rich clusters in npPd$_{1-x}$Co$_x$ prepared by GCD. All ZFC curves show a broad peak typical for blocked superparamagnetism. For assemblies of blocked superparamagnetic particles, ZFC-curves contain information about the magnetic anisotropy energy (MAE). The blocking temperature $T_{B,0}$, which can be obtained from the peak position in the ZFC curve, is a measure for the average particle volume assuming a constant anisotropy constant $K$. The blocking criterion is

$\alpha_B \approx \frac{M_{\text{min}}(T)}{M_{\text{norm}}(T)}$, where $M_{\text{min}}(T)$ is the minimum magnetization, $M_{\text{norm}}(T)$ the normalized magnetization, and $\alpha_B$ the blocking criterion. 

### TABLE I. Overview of magnetic properties and magnetization changes upon hydrogen loading for various chemical compositions of npPd$_{1-x}$Co$_x$. $x_{\text{Co,nom}}$ denotes the nominal Co content as expected from GCD, $x_{\text{Co,XRF}}$ the measured Co content via XRF, $M_{\text{min}}$ is the minimum magnetization, $\Delta M$ is the absolute variation of magnetization, $\Delta M/M_{\text{min}}$ is the relative change in magnetization, $\alpha_{C,V}$ is the magnetoelectric-voltage coefficient, as defined in Ref. 14, $T_B$ is the blocking temperature in the uncharged state, and $T_{B,H}$ is the blocking temperature in the hydrogen-charged state. The arrow indicates the increasing cluster size from top to bottom.

| $x_{\text{Co,nom}}$ (wt. %) | $x_{\text{Co,XRF}}$ (wt. %) | $M_{\text{min}}$ (emu g$^{-1}$) | $\Delta M$ (emu g$^{-1}$) | $\Delta M/M_{\text{min}}$ (%) | $\alpha_{C,V}$ (Oe V$^{-1}$) | $T_B$ (K) | $T_{B,H}$ (K) |
|--------------------------|---------------------------|----------------------|----------------------|-----------------|----------------------|---------|---------|
| 0                        | 4.9                       | 1.22                 | 0.02                 | 1.3             | 5                    | 75      | 96      |
| 3                        | 7.7                       | 1.86                 | 0.07                 | 3.8             | 19                   | 89      | 117     |
| 6                        | 11.7                      | 2.87                 | 0.22                 | 8.4             | 65                   | 103     | 167     |
| 9                        | 12.0                      | 3.67                 | 0.88                 | 24.2            | 255                  | 117     | 209     |
| 12                       | 15.7                      | 8.42                 | 0.61                 | 7.4             | 177                  | 216     | 286     |
| 15                       | 25.2                      | 13.08                | 1.50                 | 11.8            | 422                  | 265     | $\geq$300 |

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FIG. 2. Galvanodynamically controlled dealloying (GCD) of a Co75Pd25 alloy to obtain npPd(1−x)Co with variable Co content x: (a) Schematic discretization of a typical dealloying curve at constant potential (red) into static current steps of 2, 1, 0.5, and 0.1 mA. The residual Co content is controlled via adjustment of charge \(Q_x\) or, more specifically, the duration of the second etching step. (b) Co content after dealloying measured in the XRF, \(x_{\text{Co},\text{XRF}}\), as a function of the nominal Co content, \(x_{\text{Co,nom}}\), set during GCD preparation [Eq. (2)]. The error bars are given for the concentration measured in the XRF, \(x_{\text{Co},\text{XRF}}\). The red line represents a linear fit to the data points.

\[
25k_B T_B = MAE = KV,
\]

where \(k_B\) is the Boltzmann factor, \(K\) is the effective anisotropy constant for cobalt, and \(V\) is the volume of the particle. With an increase in Co concentration, blocking temperatures in Fig. 3 move from \(T_B \sim 75\) K to higher temperatures up to \(T_B \sim 265\) K (see also Table I), indicating larger magnetic clusters. Furthermore, while peaks appear sharp at low concentrations, they smear out with the increase in \(x_{\text{Co,nom}}\), pointing toward broader size distributions of magnetic clusters. This indicates that not only the size of the Co-rich clusters can be altered via GCD but also the cluster size distribution. A rough estimation of magnetic cluster sizes using Eq. (3) and a value of \(K = 4.1 \times 10^5\) J m\(^3\), which is the value for bulk hcp Co,\(^{43}\) yields average cluster diameters between \(d = 4.9\) nm (for \(T_B = 75\) K at \(x_{\text{Co,nom}} = 0\%\)) and \(d = 7.5\) nm (for \(T_B = 265\) K at \(x_{\text{Co,nom}} = 15\%\)). The magnetic tuning performance upon hydrogen charging for different superparamagnetic cluster size distributions will be covered in Sec. IV.

**IV. EFFECT OF HYDROGEN CHARGING ON THE MAGNETIC PROPERTIES**

**A. Variation of magnetization with Co content**

For npPd\(_{1-x}\)Co\(_x\) with different Co concentrations \(x_{\text{Co,nom}}\), relative variations of magnetization \(\Delta M/M_{\text{min}}\) upon hydrogen-charging and discharging are presented as a function of time \(t\) in Figs. 4(a)-4(f) and as a function of charge \(\Delta Q\) in Figs. 4(g)-4(l). Numerical values of relative changes (\(\Delta M/M_{\text{min}}\)) and absolute changes in magnetization (\(\Delta M\)) are summarized in Table I. Absolute magnetic moments were normalized to the sample weight to enable comparability. A schematic depiction of the hydrogen-charging process is shown in Fig. 1. In Figs. 4(a)-4(f), one observes a periodic variation of the magnetic moment for all compositions, with the minima/maxima occurring at the same points in time delayed with respect to the maxima/minima in applied voltage, as indicated by the gray line. However, the amplitude of the relative changes in magnetization \(\Delta M/M_{\text{min}}\) is clearly different for samples with different Co contents \(x_{\text{Co,nom}}\). One observes increasing relative variations in magnetization from \(\sim 1\%\) to \(\sim 24\%\) for increasing Co content up to \(x_{\text{Co,nom}} = 9\) wt. %. Samples at higher Co concentrations of \(x_{\text{Co,nom}} = 12\) wt. % and \(x_{\text{Co,nom}} = 15\) wt. % exhibit smaller tuning amplitudes of \(\sim 7\%\) and \(\sim 12\%\). Absolute changes in magnetization \(\Delta M\) show a similar tendency of increasing changes for higher Co content up to \(x_{\text{Co,nom}} = 9\) wt. %. At higher nominal Co concentrations, absolute change in Co concentration, blocking temperatures in Fig. 3 move from \(T_B \sim 75\) K to higher temperatures up to \(T_B \sim 265\) K (see also Table I), indicating larger magnetic clusters. Furthermore, while peaks appear sharp at low concentrations, they smear out with the increase in \(x_{\text{Co,nom}}\), pointing toward broader size distributions of magnetic clusters. This indicates that not only the size of the Co-rich clusters can be altered via GCD but also the cluster size distribution. A rough estimation of magnetic cluster sizes using Eq. (3) and a value of \(K = 4.1 \times 10^5\) J m\(^3\), which is the value for bulk hcp Co,\(^{43}\) yields average cluster diameters between \(d = 4.9\) nm (for \(T_B = 75\) K at \(x_{\text{Co,nom}} = 0\%\)) and \(d = 7.5\) nm (for \(T_B = 265\) K at \(x_{\text{Co,nom}} = 15\%\)). The magnetic tuning performance upon hydrogen charging for different superparamagnetic cluster size distributions will be covered in Sec. IV.

**FIG. 3.** Zero-field cooled (ZFC) and field cooled (FC) magnetization for npPd\(_{1-x}\)Co\(_x\) with varying Co content \(x_{\text{Co,nom}}\), charged with hydrogen (red dashed lines) and after hydrogen desorption (black solid lines). Magnetization was recorded in a field of 50 Oe. For the sake of comparability, low-temperature ZFC magnetization at \(T = 0\) was set to 0 for all curves.
first decreases slightly for $x_{\text{Co,nom}} = 12$ wt. % and then reaches with $\Delta M = 1.5 \text{ emu g}^{-1}$, the highest magnetization modulation obtained in this study for $x_{\text{Co,nom}} = 15$ wt. %. The hydrogen-induced effects on the magnetic properties were found to be volatile on larger timescales in the order of hours after removing the applied voltage, when magnetization decays exponentially (not shown). This volatility can be explained by the natural diffusion/desorption of hydrogen atoms from the Pd lattice.

**B. Variation of magnetic cluster size with Co content**

Furthermore, we measured zero-field cooling/field cooling (ZFC/FC) magnetization curves also for *in situ* hydrogen-charged samples, as depicted in Fig. 3 in red dashed curves. Hydrogen-charging has a strong effect on the shape of ZFC curves (see red dashed curves in Fig. 3): For nominal Co concentrations from $x_{\text{Co,nom}} = 0$% to $x_{\text{Co,nom}} = 12$%, the blocking temperature $T_B$ as well as the absolute values of both FC (upper branch) and ZFC (lower branch) magnetization increase considerably upon hydrogen-charging. For example, $T_B$ in the hydrogen-charged state (listed as $T_{B,H}$ in Table I) is shifted from 75 to 96 K for $x_{\text{Co,nom}} = 0$% and from 117 to 209 K for a concentration $x_{\text{Co,nom}} = 9%$. For samples with higher $x_{\text{Co,nom}}$ in (e) and (f), a shift in blocking temperature is still apparent, while changes in magnetization are less pronounced.

The most striking difference in ZFC/FC curves between the hydrogen-charged and hydrogen-discharged states is that a Co concentration of $x_{\text{Co,nom}} = 9%$ in Fig. 3 coincides with the largest relative changes in magnetization in cyclic hydrogen-charging experiments (Fig. 4). For higher Co concentrations >9% (Fig. 3), variations of both $T_B$ and $\Delta M/M_{\text{min}}$ are less prominent (compare Table I). Higher values of $T_B$ and the broad size distribution for Co concentrations >9% indicate larger magnetic clusters and suggest that there is a certain fraction of these clusters already in the ferromagnetic state. Considering that these superparamagnetic clusters are the ingredients of magneto-ionic switching here, we can interpret both relative and absolute changes in magnetization in accordance with the mean clusters sizes in the samples: With the increase in the concentration and size, superparamagnetic clusters tend closer to the ferromagnetic threshold and get easily “blocked” by the hydrogen-induced cluster coupling in a simple picture. Therefore, absolute changes in magnetization increase with the increase in the size of superparamagnetic clusters up to $\Delta M = 1.5 \text{ emu g}^{-1}$ for $x_{\text{Co,nom}} = 15%$. Existing larger ferromagnetic clusters are no longer relevant for the hydrogen-induced switching mechanism. As a certain fraction of already ferromagnetic clusters exists in npPd$_{1-x}$Co$_x$ for $x_{\text{Co,nom}} \geq 12$%, the relative tuning amplitude of magnetization is lower compared to concentrations <12%.
C. Variation of $a_{CV}$ with Co content

The curves of the relative magnetization change $\Delta M/M_{\text{min}}$ as a function of applied charge $\Delta Q$ in Figs. 4(g)-4(l) all exhibit similar lens-shaped loops regardless of composition, indicating hysteretic behavior of hydrogen absorption and desorption in npPd$_{1-x}$Co$_x$. The slope of these loops ($\Delta M/\Delta Q$) can be considered as a measure for the magnitude of the magneto-electric performance in our samples. For improved comparability with the literature, we also calculated magneto-electric coupling coefficients $a_{CV} = 4\pi \Delta M/\Delta U$ according to Ref. 14. In this new definition by Molinari et al., the voltage change $\Delta U$ is used (in our case $\Delta U = 0.5$ V) instead of the change in the electric field $\Delta E$. The reasoning behind this choice is, on one hand, practical problems with the determination of electric fields in porous materials. On the other hand, large values of the electric field at solid/electrolyte interfaces can be obtained using only small voltages in the order of Volts, which makes a comparison on the basis of electric fields to other magneto-electric devices difficult. The calculated values of $a_{CV}$ are given in Table I. The maximum value, which is $a_{CV} = 422$ Oe V$^{-1}$, is much higher compared to $a_{CV} = 18$ Oe V$^{-1}$ in our previous publication. Typical values for other ion intercalation systems range between $a_{CV} = 10$ Oe V$^{-1}$ and $a_{CV} = 1000$ Oe V$^{-1}$.

Finally, we compare magnetization changes in Table I with our prior exclusion of magneto-elastic effects. A third possible contribution to the magneto-ionic changes, which has not been covered previously, is the direct hydrogen-charging of the Co-rich clusters. Hydrogen-charging has been reported in CoPd alloys of various compositions, although the hydrogen storage capacity drops significantly below 0.1 H per Pd/Co atom, when the Co fraction is larger than 15%. As clusters in the dealloying process can be considered as relics of the original alloy, the composition of those clusters is also close to the initial alloy composition, which is Co$_{75}$Pd$_{25}$ in this work. For such Co-rich Pd alloys, it has been shown that magnetic properties remain unaffected upon hydrogen-charging, likely due to the vanishing hydrogen storage capacity at higher Co concentrations. Therefore, we still consider a hydrogen-induced change in the RKKY periodicity and a concomitant intercluster coupling, which was proposed in our previous work and in the Introduction, the most likely mechanism.

In situ electrochemical Raman spectroscopy measurements for Co-rich samples ($x = 15\%$) upon voltammetric cycling (not shown) provided no indications of a Co reduction mechanism upon hydrogen-charging, which supports our earlier conclusion of an overall unlikely oxidation-reduction mechanism. Moreover, in situ electrochemical dilatometry data (not shown) yielded no direct correlation between strain and magnetic moment, also supporting our prior exclusion of magneto-elastic effects. A different cluster size distribution in the RKKY periodicity and a concomitant intercluster coupling, which was proposed in our preceding work and in the Introduction, the most likely mechanism.

Finally, we compare magnetization changes in Table I with our preceding publication of potentiostatically dealloyed npPd(Co). One realizes that for the same lower voltage limit of $U = -0.9$ V, a higher relative change in $\Delta M/M_{\text{min}} \sim 100\%$ has been obtained in Ref. 34. These higher relative changes might be explained via the larger voltage window or a different cluster size distribution in the referenced work. The absolute value is $\Delta M = 0.15$ emu g$^{-1}$ in Ref. 34, which resides between values for Co concentrations of $x_{\text{Co,nom}} = 3\%$ and $x_{\text{Co,nom}} = 6\%$ here (see Table I for corresponding values of $x_{\text{Co,XRF}}$). Considering the Co concentration of $x_{\text{Co,XRF}} = 7.2\%$, measured for potentiostatically dealloyed npPd(Co), absolute changes in $\Delta M$ roughly follow the trend with the Co concentration for GCD.

V. CONCLUSION

In this study, we analyzed the effect of Co-concentration in npPd$_{1-x}$Co$_x$ on the magnetic tuning response upon hydrogen charging. In situ electrochemical hydrogen-charging allowed direct insights into the interaction of hydrogen with superparamagnetic Co-rich clusters, suggesting that magnetic anisotropy energy of the Co-rich clusters, which scales with the volume of the Co clusters,
is strongly modified by hydrogen atoms. An ideal Co concentration of $x_{\text{Co,room}} \approx 9\%$ yielded the highest relative changes in magnetization, while the maximum Co concentration ($x_{\text{Co,room}} \approx 15\%$ in this work) produced the largest absolute change in magnetization of $\Delta M = 1.5 \text{ emu g}^{-1}$. Temperature-dependent magnetization curves revealed a strong hydrogen-induced upshift of superparamagnetic blocking temperatures, which proves a modification of the magnetic anisotropy energy induced by hydrogen atoms. Our results offer intriguing possibilities for the conception of novel magneto-electric devices, utilizing a voltage-induced blocking of superparamagnetic entities.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

1. K. T. Moller, T. R. Jensen, E. Akiba, and H.-W. Li, "Hydrogen—A sustainable energy carrier," Prog. Nat. Sci.: Mater. Int. 27, 34–40 (2017).
2. S. Sakintuna, F. Lamari-Darkrim, and M. Hirscher, “Metal hydride materials for solid hydrogen storage: A review," Int. J. Hydrogen Energy 32, 1121–1140 (2007).
3. A. Züttel, "Hydrogen storage methods,” Naturwissenschaften 91, 157–172 (2004).
4. J. C. Barton, J. A. S. Green, and F. A. Lewis, "Changes of electrode potential and electrical resistance as a function of the hydrogen content of some Pd + Ni and Pd + Rh alloys," Trans. Faraday Soc. 62, 960–970 (1966).
5. J. N. Huiberts, R. Griessen, J. H. Rector, R. J. Wyjgaardena, J. Dekker, D. G. de Groot, and N. J. Koeman, "Yttrium and lanthanum hydride films with switchable optical properties," Nature 380, 231–234 (1996).
6. T. P. Leervad Pedersen, C. Liesch, C. Salinka, T. Eleftheriadis, H. Weiss, and M. Wuttig, "Hydrogen-induced changes of mechanical stress and optical transmission in thin Pd films," Thin Solid Films 458, 299–303 (2004).
7. P.-C. Chang, T.-H. Chiang, D.-H. Wei, and W.-C. Lin, "Thermally modulated hydrogenation in Fe$_{1-x}$Pd$_x$ alloy films: Temperature-driven peculiar variation of magnetism," Appl. Phys. Lett. 116, 102407 (2020).
8. S. Akamaru, A. Kimura, M. Hara, K. Nishimura, and T. Abe, "Hydrogenation effect on magnetic properties of Pd-Co alloys," J. Magn. Magn. Mater. 484, 8–13 (2019).
9. T. Graham, "On the relation of hydrogen to palladium," Proc. R. Soc. London 17, 212–220 (1869).
10. M. Shao, "Palladium-based electrocatalysts for hydrogen oxidation and oxygen reduction reactions," J. Power Sources 196, 2433–2444 (2011).
11. S. K. Konda and A. Chen, "Palladium based nanomaterials for enhanced hydrogen spillover and storage," Mater. Today 19, 100–108 (2016).
12. E. Antolini, "Palladium in fuel cell catalysis," Energy Environ. Sci. 2, 915–931 (2009).
13. C. Navarro-Senten, A. Quintana, E. Menéndez, E. Pellicer, and J. Sort, “Electrolyte-gated magnetoelectric actuation: Phenomenology, materials, mechanisms, and prospective applications,” APL Mater. 7, 030701 (2019).
14. M. Molinari, H. Hahn, and R. Krük, “Voltage-control of magnetism in solid-state and solid/liquid magnetoelectric composites,” Adv. Mater. 31, 1806662 (2019).
15. K. Leistner, “Electrochemical approaches to room temperature magnetoelectric materials,”Curr. Opin. Electrochem. 25, 100636 (2021).
16. J. Zehner, I. Soldatov, S. Schneider, R. Heller, N. B. Khojasteh, S. Schiemenz, S. Fähler, K. Niesch, R. Schäfer, and K. Leistner, “Voltage-controlled deblocking of magnetization reversal in thin films by tunable domain wall interactions and pinning sites,” Adv. Electron. Mater. 6, 2009406 (2020).
17. M. Nichterwitz, S. Honnali, J. Zehner, S. Schneider, D. Pohl, S. Schiemenz, S. T. B. Goennerwein, K. Niesch, and K. Leistner, “Control of positive and negative magnetoresistance in iron oxide-iron nanocomposite thin films for tunable magnetoelectric nanodevices,” ACS Appl. Electron. Mater. 2, 2543–2549 (2020).
18. J. de Rojas, A. Quintana, A. Lopeandia, J. Salguero, J. L. Costa-Krämer, L. Abad, M. O. Liedke, M. Butterling, A. Wagner, L. Henderick, J. Dendooven, C. Detavernier, J. Sort, and E. Menéndez, “Boosting room-temperature magnetoelectrics in a non-magnetic oxide semiconductor,” Adv. Funct. Mater. 30, 2002704 (2020).
19. P. Maroun, F. Reikowski, N. Di, T. Wiegmann, J. Stettner, O. M. Magnusson, and P. Allongue, “Potential dependence of the structure and magnetism of electrodeposited Pd/Co/Au(111) layers,” J. Electrochem. Soc. 819, 322–330 (2018).
20. D. A. Gilbert, J. Olamit, R. K. Dumas, B. J. Kirby, A. J. Grutter, B. B. Maranville, E. Arenholz, J. A. Borchers, and K. Liu, “Controllable positive exchange bias via redox-driven oxygen migration,” Nat. Commun. 7, 11050 (2016).
21. T. Traufing, S. Topolovec, K. Nadeem, D. Vinga Szabó, H. Krenn, and R. Würschum, “Magnetization of Fe$_3$O$_4$ based nanocomposite tuned by surface charging,” Phys. Status Solidi RRL 5, 150–152 (2011).
22. S. Topolovec, P. Jerabek, D. V. Szabó, H. Krenn, and R. Würschum, “SQUID magnetometry combined with in situ cyclic voltammetry: A case study of tunable magnetism of γ-Fe$_3$O$_4$ nanoparticles,” J. Magn. Magn. Mater. 329, 43–48 (2013).
23. S. Gholsh, “Switching magnetic order in nanoporous Pd-Ni by electrochemical charging,” J. Mater. Res. 28, 3010–3017 (2013).
24. A. Nicoleno, C. Navarro-Senten, and J. Sort, “Nanoporous composites with converse magnetoelectric effects for energy-efficient applications,” in Reference Module in Materials Science and Materials Engineering (Elsevier, 2021).
25. S. Robbenrott, P. Yu, A. Nicoleno, P. Mercier Fernandez, M. Coll, and J. Sort, “Magnetico-ionic control of magnetism in two-oxide nanocomposite thin films comprising mesoporous cobalt ferrite conformally nanocoated with HfO$_2$,” Nanoscale 12, 5987–5994 (2020).
26. C. Navarro-Senten, A. Quintana, E. Isarain-Chávez, E. Weschke, P. Yu, M. Coll, E. Pellicer, E. Menéndez, and J. Sort, “Enhancing magneto-ionic effects in magnetic nanostructured films via conformal deposition of nanolayers with oxygen acceptor/donor capabilities,” ACS Appl. Mater. Interfaces 12, 14484–14494 (2020).
27. M. Nichterwitz, S. Neitsch, S. Röther, D. Wolf, K. Nielsch, and K. Leistner, “Voltage-controlled ON switching and manipulation of magnetization via the redox transformation of β-FeOOH nanoplatelets,” J. Phys. D: Appl. Phys. 53, 084001 (2019).
28. Q. Zhang, X. Luo, L. Wang, L. Zhang, R. Khalid, J. Gong, and H. Wu, “Lithium-ion battery cycling for magnetism control,” Nano Lett. 16, 583–587 (2016).
29. G. Klinser, S. Topolovec, H. Krenn, and R. Würschum, “Process monitoring of charging/discharging of lithium ion battery cathodes by operando SQUID magnetometry,” in Encyclopedia of Interfacial Chemistry, edited by K. Wandelt (Elsevier, Oxford, 2018), pp. 849–855.
30. K. Taniguchi, K. Narushima, H. Sagayama, W. Kosaka, N. Shito, and H. Miyasaka, “In situ reversible ionic control for nonvolatile magnetic phases in a donor/acceptor metal-organic framework,” Adv. Funct. Mater. 27, 1604990 (2017).
31. S. Daugupta, B. Das, Q. Li, D. Wang, T. T. Baby, S. Indris, M. Knapp, H. Ehrenberg, K. Fink, R. Krük, and H. Hahn, “Toward on-and-off magnetism: Reversible...

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electrochemistry to control magnetic phase transitions in spinel ferrites,” Adv. Funct. Mater. 26, 7507–7515 (2016).
32 G. Klinser, R. Zettl, M. Wilkening, H. Krenn, I. Hanzu, and R. Würschum, “Redox processes in sodium vanadium phosphate cathodes—Insights from operando magnetometry,” Phys. Chem. Chem. Phys. 21, 20151–20155 (2019).
33 S. Vasala, A. Jakob, K. Wissel, A. I. Waidha, L. Alff, and O. Clemens, “Reversible tuning of magnetization in a ferromagnetic Ruddlesden-Popper-type manganite by electrochemical fluoride-ion intercalation,” Adv. Electron. Mater. 6, 1900974 (2020).
34 M. Gößler, M. Albu, G. Klinser, E.-M. Steyskal, H. Krenn, and R. Würschum, “Magneto-ionic switching of superparamagnetism,” Small 15, 1904523 (2019).
35 X. Ye, H. K. Singh, H. Zhang, H. Geßwein, M. R. Chellali, R. Witte, A. Molinari, K. Skokok, O. Gutfleisch, H. Hahn, and R. Kruck, “Giant voltage-induced modification of magnetism in micron-scale ferromagnetic metals by hydrogen charging,” Nat. Commun. 11, 4849 (2020).
36 M. Enyo and P. C. Biswas, “Hydrogen absorption in palladium electrodes in alkaline solutions,” J. Electroanal. Chem. 335, 309–319 (1992).
37 G. Andreasen, A. Visintin, R. C. Salvarezzza, W. E. Triaca, and A. J. Arvia, “Hydrogen-induced deformations of metals followed by in situ scanning tunneling microscopy. Palladium electrolytic hydrogen charging and discharging in alkaline solution,” Langmuir 15, 1–5 (1999).
38 H. K. D. Kim, L. T. Schelhas, S. Keller, J. L. Hockel, S. H. Tolbert, and G. P. Carman, “Magnetoelectric control of superparamagnetism,” Nano Lett. 13, 884–888 (2013).
39 A. Lackmann, M. Bäumer, G. Wittstock, and A. Wittstock, “Independent control over residual silver content of nanoporous gold by galvano-dynamically controlled dealloying,” Nanoscale 10, 17166–17173 (2018).
40 S. Topolovec, H. Krenn, and R. Würschum, “Electrochemical cell for in situ electrodeposition of magnetic thin films in a superconducting quantum interference device magnetometer,” Rev. Sci. Instrum. 86, 063903 (2015).
41 S. Topolovec, H. Krenn, and R. Würschum, “Enhanced magnetic moment of ultrathin Co films measured by in situ electrodeposition in a SQUID,” J. Magn. Magn. Mater. 397, 96–100 (2016).
42 M. Gößler, M. Nachtnebel, H. Schröttner, H. Krenn, E.-M. Steyskal, and R. Würschum, “Evolution of superparamagnetism in the electrochemical dealloying process,” J. Appl. Phys. 128, 093904 (2020).
43 J. M. D. Coey, Magnetism and Magnetic Materials (Cambridge University Press, 2010), pp. 264–304.
44 K. Klyukin, G. Beach, and B. Yildiz, “Hydrogen tunes magnetic anisotropy by affecting local hybridization at the interface of a ferromagnet with nonmagnetic metals,” Phys. Rev. Mater. 4, 104416 (2020).
45 A. J. Tan, M. Huang, C. O. Avci, F. Böttner, M. Mann, W. Hu, C. Mazzoli, S. Wilkins, H. L. Tuller, and G. S. D. Beach, “Magneto-ionic control of magnetism using a solid-state proton pump,” Nat. Mater. 18, 35–41 (2019).
46 K. Munbodh, F. A. Perez, C. Keenan, D. Lederman, M. Zhernenkov, and M. R. Fitzsimmons, “Effects of hydrogen/deuterium absorption on the magnetic properties of Co/Pd multilayers,” Phys. Rev. B 83, 094432 (2011).
47 K. Munbodh, F. A. Perez, and D. Lederman, “Changes in magnetic properties of Co/Pd multilayers induced by hydrogen absorption,” J. Appl. Phys. 111, 123919 (2012).
48 A. Hillaert, A. Tamion, F. Tournus, C. Albin, and V. Dupuis, “From vanishing interaction to superferromagnetic dimerization: Experimental determination of interaction lengths for embedded Co clusters,” Phys. Rev. B 95, 134446 (2017).
49 D. Wang, K.-Y. Lee, S. Luo, and T. B. Flanagan, “The thermodynamics of hydrogen absorption/desorption by Pd-Co alloys,” J. Alloys Compd. 252, 209–218 (1997).
50 T. Krekeler, A. V. Straßer, M. Graf, K. Wang, C. Hartig, M. Ritter, and J. Weissmüller, “Silver-rich clusters in nanoporous gold,” Mater. Res. Lett. 5, 314–321 (2017).
51 W.-C. Lin, B.-Y. Wang, H.-Y. Huang, C.-J. Tsai, and V. R. Mudinepalli, “Hydrogen absorption-induced reversible change in magnetic properties of Co–Pd alloy films,” J. Alloys Compd. 661, 20–26 (2016).