# Climbing the Hydrogen Evolution Volcano with a NiTi Shape Memory Alloy

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**ABSTRACT:** Alkaline water electrolysis is a sustainable way to produce green hydrogen using renewable electricity. Even though the rates of the cathodic Hydrogen Evolution Reaction (HER) are two to three orders of magnitude less in alkaline compared to acidic conditions, the possibility of using non-precious catalysts makes alkaline HER appealing. We identify a novel and facile route for substantially improving HER performance via the use of commercially available NiTi shape memory alloys, which upon heating undergo a phase transformation from the monoclinic martensite to cubic austenite structure. While room temperature performance is modest, austenitic NiTi outperforms in terms of current density Pt (which is the state-of-the-art HER electrocatalyst) by up to 50 % at 80 °C. Surface ensembles presented by the austenite phase are computed with density functional theory to bind hydrogen more weakly than either metallic Ni or Ti and to have binding energies ideally suited for HER.



E<sub>M-H, binding</sub>

Hydrogen has the potential to be an eco-friendly, carbon-neutral energy carrier, and therefore water electrolysis has gained much attention in research in recent times.<sup>1–4</sup> Although a large body of work focuses on the more complicated 4-electron oxygen evolution reaction (OER)<sup>5,6</sup>, the 2-electron hydrogen evolution reaction (HER) presents its own challenges, especially under alkaline conditions relevant to alkaline and anion exchange membrane water electrolysis.<sup>7–12</sup> Under alkaline conditions the free proton density is nearly zero; therefore the initial Volmer step depends on water dissociation (H<sub>2</sub>O + e<sup>-</sup>  $\rightarrow$  OH<sup>-</sup> + H<sub>ads</sub>) to provide the free proton for the reaction to proceed via a Heyrovsky or a Tafel step.<sup>2,5,8,13,14</sup> The Heyrovsky step (H<sub>ads</sub> + H<sub>2</sub>O + e<sup>-</sup>  $\rightarrow$  H<sub>2</sub> + OH<sup>-</sup>) also depends on the water dissociation step at the interface. Additionally, in both Volmer and Heyrovsky steps, OH<sup>-</sup> is produced at the expense of water, thus shifting the reaction equilibria to the left. As a result, HER is more energy-intensive in alkaline than in acidic media.<sup>2</sup> However, the possibility of using non-precious metal-based catalysts, unlike in acidic electrolytes, makes alkaline HER a system of primary practical importance.<sup>7,13</sup>

The HER activities of electrocatalysts can be correlated with their hydrogen-binding energy via a volcano-type relationship, revealing that optimal binding energy is necessary to obtain the highest activity for hydrogen evolution.<sup>15</sup> Such relationships provide important insight into designing cost-effective and highly efficient catalysts able to meet future energy demands. Apart from the benchmark platinum group metal-based catalysts, catalysts prepared from earth-abundant materials, mainly Ni, are effective for alkaline HER.<sup>16</sup> Ni itself, however, has insufficient electrocatalytic activity and poor durability associated with the formation of nickel hydride on the electrode surface, especially during prolonged cathodic polarization in the alkaline electrolyte.<sup>17–20</sup> Ni forms strong hydrogen bonds and is unable to desorb OH<sup>-</sup> species, hindering further water dissociation.<sup>18,20–22</sup>

Alloying Ni with other metals has proved to be a viable strategy for improving electrocatalytic performance. Jaramillo *et al.* showed that the HER activity of binary metal alloys NiMo, NiMoCo, CoMo, NiFe, and NiMoFe exceed Ni in 1 M NaOH.<sup>23</sup> The high performance of these alloys is attributed to electronic synergy between Ni and adjacent heteroatoms that improves surface adsorption properties. The Ni is believed to promote water dissociation and the alloying of transition metals with empty or less-filled d orbitals (e.g. Mo) believed to improve adsorption properties towards hydrogen.<sup>21</sup>

Strain regulation is an alternative approach to altering catalyst properties, enabling selective tuning of geometric and electronic structure.<sup>24</sup> For instance, heteroatom doping can induce significant lattice mismatch and thus introduce strain to promote HER reactions. Chen *et al.* developed Pt<sub>3</sub>Ni nanoframes, which due to the surface strain effect, showed enhanced HER performance under alkaline conditions compared to commercial Pt/C catalysts.<sup>25</sup> In a similar direction, Wang *et al.* demonstrated that a highly compressive strained surface of Ru@Pt core-shell nanostructure exhibited higher HER activity than the strain-free Ru-Pt alloy, where the strain effect decreases the energy barrier for H<sub>ads</sub> desorption, which is the rate limiting step.<sup>26,27</sup> Overall, the fabrication of strain-engineered catalysts relies typically on the use of core-shell structures and elastic substrates. However, the development of such catalytic systems is labor-intensive, since several fabrication aspects need to be considered to maximize the strain-activity correlation.<sup>28</sup>

We report here the observation of the high HER performance of a NiTi shape memory alloy (SMA). At room temperature, NiTi exists in the monoclinic martensite phase, transforming into the simple-cubic austenite phase upon heating.<sup>29,30</sup> Shape memory effects emerge from the martensitic transformation from austenite to martensite on cooling and the reverse transformation on heating.<sup>31,32</sup> The SMA properties of NiTi potentially offer a unique and unexplored handle to control electrochemical properties and open new routes for tuning performance. To the best of our knowledge, the only examination of SMAs in electrochemical systems was reported by Muralidharan *et al.*, who used the superelastic properties of a NiTi substrate to tune the properties of a Ni-Ti-O electrocatalyst through induced mechanical strain.<sup>33</sup>

Herein we investigate the alkaline HER performance of a nearly equiatomic NiTi SMA. We observe the electrocatalytic performance to have a large temperature dependence that can be traced to changes in the material phase. At 80 °C, when the austenite phase is predominant, area-normalized HER activity exceeds that of Pt by up to 50 %, thus offering a very promising, scalable and cost-effective alternative for the cathode of alkaline water electrolyzers. To identify the origins of this behavior, we report density functional theory (DFT) and HER activity models to determine the expected performance of the NiTi phases. Results identify an ensemble exposed by the low-energy surface of the austenite phase that has an optimal hydrogen binding energy and rationalizes the strong temperature dependence observed.



**Figure 1**. (A) Rietveld refinement of the XRD data of NiTi wire at 20 °C and 80 °C. Black dots are the experimental data points, red and green solid lines are the refinements and the grey lines are the residuals. The red tick marks indicate the expected Bragg peak position for the Austenite phase and the blue ticks for the Martensite phase and (B) HRTEM and (B1-B2) interplanar distances and Fast Fourier Transform partner of the selected areas (inset) of NiTi wire at 20 °C.

We used commercial NiTi wires (details given in Supplementary Information) of 2 mm diameter. The use of commercial wire samples facilitates reproduction of our results by others and allows direct comparison with Ni, Ti and Pt electrocatalysts without introduction of effects related to differences in surface area and/or particle size. Prior to electrochemical analysis, the sample was characterized by synchrotron X-ray diffraction in 20 °C increments from 20 to 80 °C, to evidence the SMA phase transformation upon heating. This temperature range was

selected as representative of the typical operating range of alkaline and AEM water electrolyzers. Experimental details are available in the Supplementary Information. A comparison of the XRD patterns with corresponding Rietveld refinement at 20 and 80 °C is shown in Figure 1A while those of the intermediate temperatures (40 and 60 °C) are shown in Figure S1A. With increasing temperature, the peak intensities change with the material phase transition. Two structures with cubic (austenite) and monoclinic (martensite) symmetry coexist at 20 and 40 °C. This phase coexistence at low temperatures was also confirmed by HRTEM (Figure 1B). Upon heating, the martensite (major phase) NiTi transforms completely to its cubic (austenite) phase. Only the cubic phase remains at temperatures above 60 °C. Figure S1B shows the normalized XRD peak intensities at 1.38 nm<sup>-1</sup> and 4.13 nm<sup>-1</sup> corresponding to the martensite and austenite phases, respectively, to illustrate the phase transition as a function of temperature.<sup>34</sup> The onset of the major phase transformation is at around 40 °C, which is consistent with literature that correlates the Ni/Ti ratio (in our case Ni (at %) ~ 50.2) with the phase transition temperature.<sup>31</sup> As a reference, the XRD patterns of Ti, Ni and Pt wires at 20 °C are shown in Figure S1C.

The electrocatalytic activity of the NiTi SMA wire towards HER was assessed in 1 M KOH electrolyte at temperatures 20, 40, 60 and 80 °C (Figure 2A). Experiments with conventional, monometallic wires of Ni, Ti and Pt were also performed for comparison (Figure 2B-D). Experimental details are available in Supplementary Information. To exclude the potential contributions of differential surface area changes to differences in activity, the electrochemically active surface area (ECSA) of NiTi samples was determined at all temperatures (Figure S2). The ECSAs at 40, 60 and 80 °C are respectively 1.1, 1.4 and 1.6 times larger than the ECSA at 20 °C. On the other hand, the current densities at -0.4 V at 40, 60 and 80 °C are respectively 1.5, 2 and 3.3 times larger than that at 20 °C. We conclude that the experimentally observed HER enhancement with temperature is not due solely to an increase in ECSA. Rather, there is a significant intrinsic catalytic activity change of the electrocatalyst. Further characterization of the samples (SEM and XPS) has been performed before and after the electrochemical testing and explained in the SI (Figures S3 and S4).

These experiments reveal three key observations, the phenomenology of which will be analyzed further below.

- At high overpotentials, the NiTi electrocatalyst outperforms all monometallic samples, including the benchmark Pt wire (which is the state-of-the-art HER electrocatalyst)<sup>23</sup>, across the entire temperature range.
- The temperature-dependent HER activity of NiTi is much stronger than that observed with the monometallic wires. As a result, exceptionally high current densities were obtained with NiTi at 80 °C, reaching 445 mA cm<sup>-2</sup> at -0.4 V (vs RHE) vs 290 mA cm<sup>-2</sup> with Pt.
- The potential-dependent HER activity of NiTi is different from Pt, the distinctions becoming clear with temperature changes. Figures 2E and F highlight the comparison between NiTi and Pt wires. Results suggest that at far from equilibrium conditions (i.e. high overpotentials, Figure 2E) NiTi outperforms Pt across the entire temperature range, whereas this is not the case at close-to-equilibrium conditions (i.e. low overpotentials, Figure 2F). Specifically, to drive a small current density of 10 mA cm<sup>-2</sup>, NiTi requires more

overpotential than Pt at low temperatures, almost equal overpotential to Pt at 60 °C and less overpotential than Pt at 80 °C.



**Figure 2**. Electrocatalytic performances towards HER in 1 M KOH. Polarization curves of (A) NiTi, (B) Ni, (C) Ti and (D) Pt wires at different temperatures presenting different overpotentials at a current density of 10 mA cm<sup>-2</sup>, (E) Comparison between electrocatalytic activities of NiTi and Pt at different temperatures and (F) Comparison between the overpotentials measured at 10 mA cm<sup>-2</sup> for NiTi, Ni and Pt. All potentials are *iR* corrected and measured *vs* Reversible Hydrogen Electrode (RHE).

The significance of these observations is evident from a comparison with the literature,<sup>23</sup> using as a commonly accepted metric the overpotential needed to reach 10 mA cm<sup>-2</sup>. The overpotential for a high-performance Pt electrocatalyst is 110 mV, close to the 100 mV value reported for a rotating disk Pt electrode at room temperature. As the temperature increases, the overpotential value decreases to 95, 86 and 81 mV at 40, 60 and 80 °C, respectively, reflecting improved kinetics. The same analysis for NiTi leads to overpotential values of 220, 149, 101 and 62 mV for 20, 40, 60 and 80 °C, respectively (Figure 2).

It is worth mentioning here that increased operating temperature leads to reduced kinetics losses due to improved reaction and transport kinetics.<sup>35</sup> Thus the effect of temperature on the electrode performance will be beneficial beyond the phase transformation temperature. Electrochemical impedance spectroscopy (EIS) data for the NiTi as a function of temperature are provided in Figure S5 and Table S1.

The short-term performance and stability of the NiTi electrocatalyst at different temperatures were investigated by chronopotentiometry at a current density of 10 mA cm<sup>-2</sup> for 9 h in 1 M KOH, as shown in Figure S6(A). The Faradaic efficiency as determined *via* gas chromatography is greater than 92 %, thus excluding contributions of side electrochemical reactions (Figure S6(B)). NiTi at 80 °C has ~200 mV lower overpotential at 10 mA cm<sup>-2</sup> (see Figure S6(C) for 100 mA cm<sup>-2</sup>) than that of NiTi@20 °C, consistent with the phase transition

enhancing the electrocatalytic activity of NiTi. Small changes in potential were observed (it is worth noting that for the case of 80 °C, the slight increase of the overpotential is due to the gradual evaporation of the electrolyte that leads to a decrease of the electrode surface area in the electrolyte), showing that the electrodes are very stable and do not suffer severe degradation over 9 h.

NiTi at 80 °C has ~200 mV lower overpotential than that of NiTi@20 °C, suggesting that the appearance of the austenite phase is associated with an enhancement in electrocatalytic activity. To rationalize the strong temperature dependence of the HER activity, we turned to DFT calculations (detailed in SI) to compare the expected HER activity of the two NiTi phases. Previous work<sup>15</sup> shows that the hydrogen adsorption energy ( $E_{\text{H-ads}}$ ) is a good descriptor of alkaline HER activity. Following the approach of Nørskov *et al.*<sup>36</sup>, the  $E_{\text{H-ads}}$  of representative strong-binding (Ni, Ti) and more noble (Ag, Au) metals (Table S2, Eq. S1) spanning the HER volcano were calculated. As shown in Figures 3 and S7 and Table S3, both metallic Ni and Ti lie on the left side of the DFT-computed HER volcano plot, accommodating H too strongly to be effective catalysts, while Ag and Au lie on the right, binding H too weakly at attract H.  $E_{\text{H-ads}}$  on various facets of the two known NiTi phases (Table S4, Figure S8) were considered.

Both XRD analysis (Figure 1A) and DFT surface energy calculations (Table S5, Figure S9, Eq. S2) informed the choice of facets; crystallographic planes with high XRD intensity and relatively low surface energy were considered as candidate model surfaces, including the Austenite (110) and (211) and Martensite (111) and (001) facets. Figures 3(A-D) provide top views of these facets and candidate H-adsorption sites labeled A-G. The tabulated values of the energies shown in Figure 3 can be found in Table S6. As shown in Table S7, H adsorption energies per site are sensitive to facet and site, and a number of sites have adsorption energies that are near the peak of the HER volcano. Thus, sites with "optimal"  $E_{\text{H-ads}}$ , allowing for high catalytic turnover, are present in both phases. However, these optimal adsorption sites are not the sites with the strongest (i.e. most negative)  $E_{\text{H-ads}}$ . The strongest  $E_{\text{H-ads}}$  sites of Austenite are near Ni and those of Martensite are even lower on the HER volcano. These low-energy sites will be populated preferentially under HER conditions.

To account for the populations of multiple sites under HER conditions, we identified distinct combinations of adsorption sites and computed formation energies relative to clean surfaces. Results for the four facets vs area-normalized H coverage are shown in Figures 3 (E-H); each point corresponds to a different coverage and/or H arrangement. The low energy hulls are indicated with lines, and the slopes of the hulls are used to extract differential  $E_{\text{H-ads.}}$ . On Austenite (110), for instance, the  $\alpha$  region corresponds to the filling of 'B' sites with an H atom;  $\beta$  corresponds to the filling of site 'A' after site 'B' is H-saturated, similarly for other facets. The differential energies are imposed on the HER volcano as dashed lines in Figures 3(I-L). On Austenite (110), under HER conditions all 'B' sites are expected to be filled, and HER turnover will be associated with the 'A' sites. Based on the location of the  $\alpha$  region on the volcano plot, 'A' sites are expected to have exceptionally high HER activity, consistent with observation. On Austenite (211), the  $\delta$  state is expected to have the highest catalytic activity. In contrast, the (001) Martensite facet has no sites suitable to support HER, and only the  $\delta$  region of the (111) facet of Martensite is expected to have appreciable HER activity. The high activity of the high temperature Austenite phase thus appears to be a consequence of the

low energy of the (110) facet and the high density of "optimal" sites on that facet. In contrast, the lowest surface energy Martensite (111) facet presents a lower density of less optimal sites, hence lower HER activity.



**Figure 3.** Top views of the NiTi (A) Austenite (110), (B) Austenite (211), (C) Martensite (111) and (D) Martensite (001) surfaces, with supercell boundaries indicated in black, candidate hydrogen adsorption sites represented as white spheres, and symmetry-distinct sites indicated with letter labels. (E) DFT computed formation energies vs H coverage and configuration on the Austenite (110) surface; solid lines connect the low energy hull. Distinct coverage domains are indicated with Greek letters. (F, G and H) are similar to (E) for Austenite (111), Martensite (001) and Martensite (111) respectively. (I) Exchange current densities<sup>37</sup> vs RPBE H binding energies on metals (dots) and extracted from the slopes of the corresponding Austenite (110) hull (red vertical dashed lines). (J, K, and L) similar to (I) for Austenite (111), Martensite (001) and Martensite (111) respectively.

We used standard analysis to compute the Tafel plots for Pt(111) and the optimal Martensite (111) and Austenite (110) sites. As shown in SI (Eq. S3-4, Tables S8-9 and Figures S10-12), the closer approach of the Austenite sites to the volcano maximum is consistent with the greater temperature dependence. To approximate the contributions of composition change with temperature, we computed and compared synthetic Tafel plots of materials of varying composition and compared with observed results. Observations are best rationalized by a material that is Martensite-rich at 20 °C, with increasing Austenite composition with increasing temperature, and that is Austenite at 80 °C (SI Figure S12).

Alloying and strain are two common ways of modifying (electro)catalytic performance. Here we examined the performance of a commercial and nearly equiatomic NiTi shapememory alloy towards hydrogen evolution reaction in an alkaline medium at temperatures in the martensitic and austenitic regions. The performance of the alloy exceeds that expected of either alloying element at 20 °C. DFT calculations suggest that some sites on the martensite domain have binding energies similar to those on Pt, but that these sites will be of relatively low density, leading to performance less than Pt. Area-normalized performance at 80 °C exceeds that of Pt (which is the state-of-the-art HER electrocatalyst)<sup>23</sup> by 50%. This performance is associated with transformation to a pure austenite phase. DFT calculations indicate that the low-energy facet of Austenite presents a high density of sites with optimal H binding characteristics. Thus, both alloying and the strain associated with transformation to Austenite contribute to its high performance. Overall, our findings suggest that this class of materials is promising for alkaline and anion exchange membrane-based electrolysis processes and beyond.

### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXXX. This file contains an experimental section, materials information, characterization techniques (XRD, XPS, EIS), HER activity comparison plots, Tafel plots, and plots for ECSA and SEM images, bulk structures of two NiTi phases and slab structures as well as extensive information about the DFT calculations.

**Data Availability:** The data that support the findings of this study are openly available in Zenodo at https://doi.org/10.5281/zenodo.8224051.

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### Notes

A European patent application, based on results from this work, has been filed by DIFFER and Toyota Motor Europe Corporation.

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