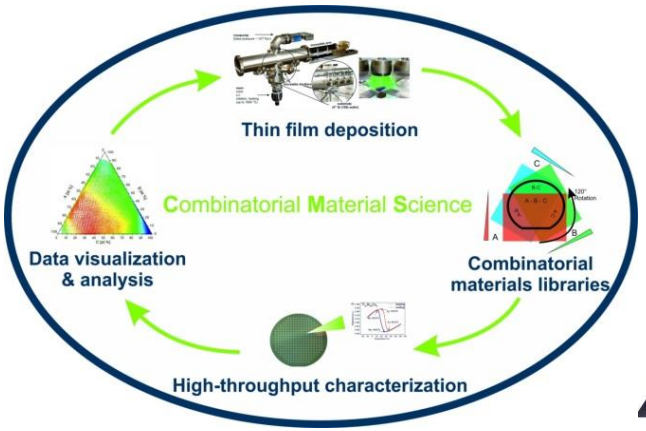
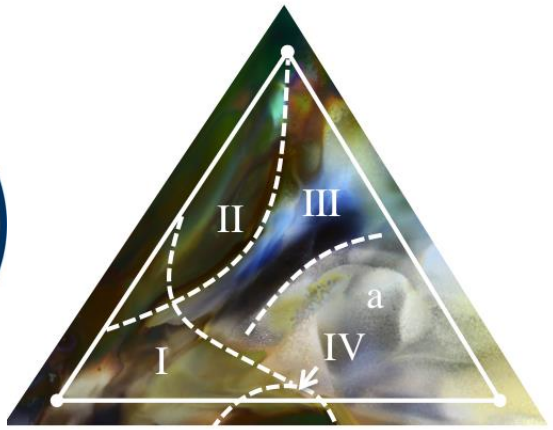
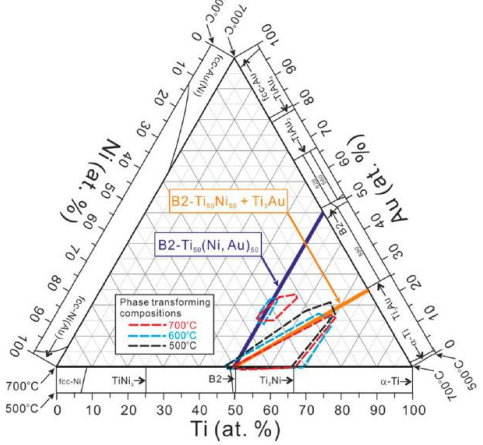






RUB

RUHR-UNIVERSITÄT BOCHUM

Fundamental Aspects of Materials Science and Engineering

Summer term 2025: Update Lecture

Multinary Phases

Prof. Dr.-Ing. Alfred Ludwig

Materials Discovery and Interfaces

Multinary phases

Unexplored compositionally complex alloys

Compositionally complex alloys: > 4 elements

Steels

Superalloys

High-entropy alloys

Multiple principal element alloys

Metallic glasses

….

Number of combinations of n=50 elements

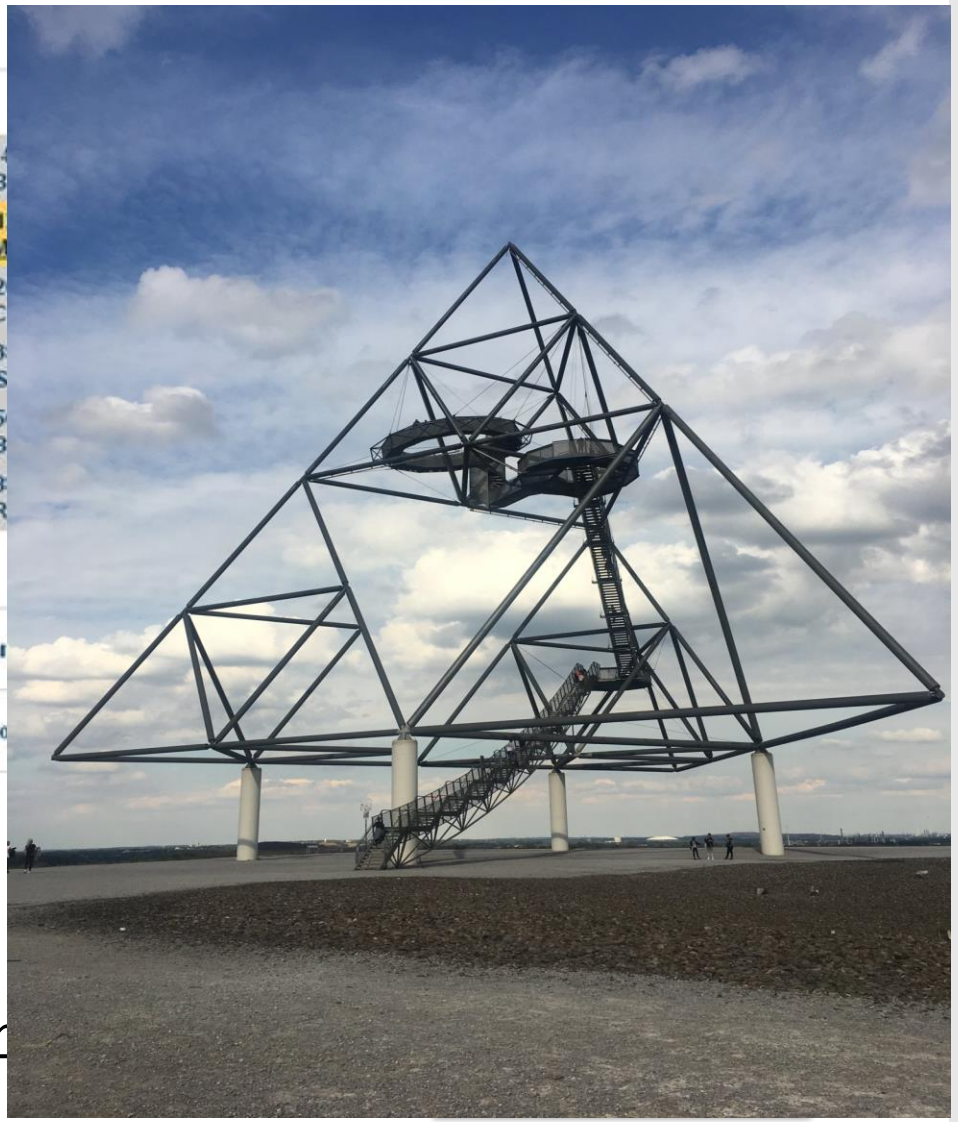
$(n/k) = n!/(k!(n-k)!)$

Binaries: 1225

Ternaries: 19600 (information on 7380 systems)

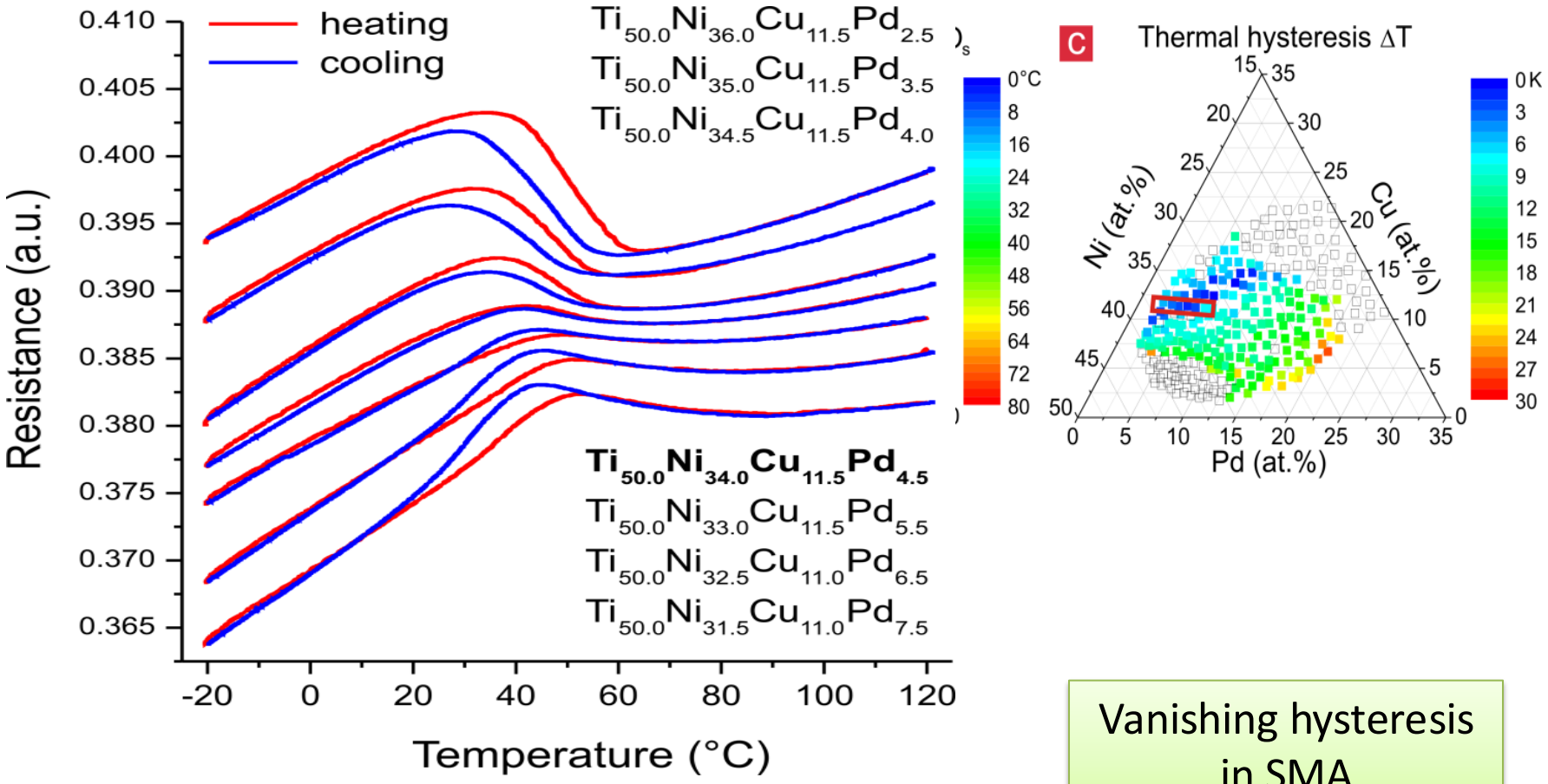
Quaternaries: 230000

Quinaries: 2.118.760



“Combinatorial explosion” for r

Exemplaric results for intermetallic systems: Quaternary shape memory alloys



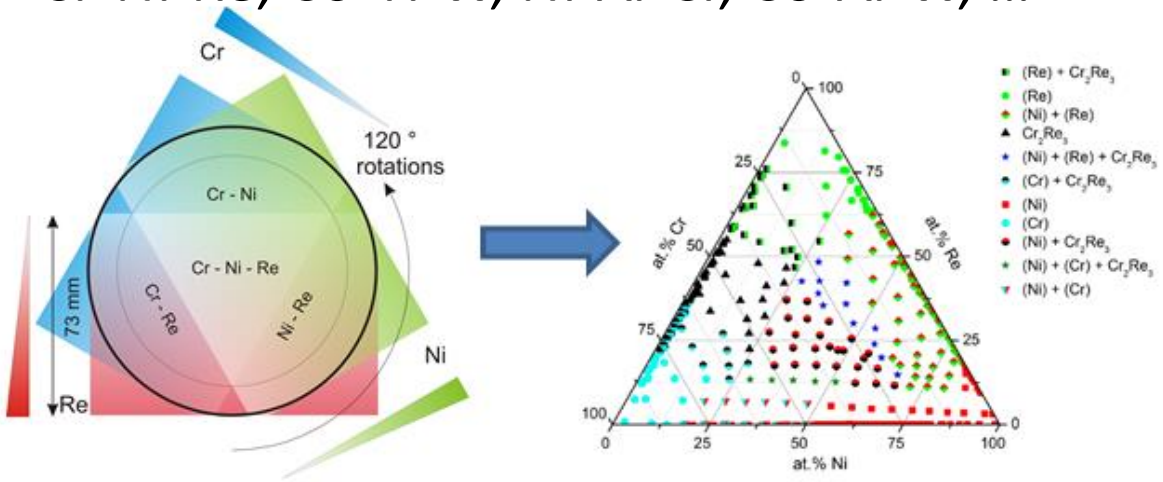
Vanishing hysteresis in SMA

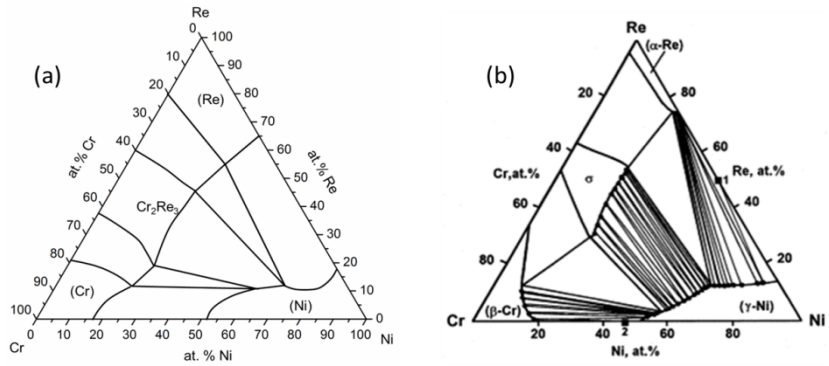
Prof. Dr.-Ing. A. Ludwig | www.rub.de/wdm | R. Zarnetta, R. Takahash, V. Srivastava, M. L. Young, A. Savan, Y. Furuya, S. Thienhaus, B. Maaß, M. Rahim, J. Frenzel, H. Brunken, Y. S. Chu, R. D. James, I. Takeuchi, G. Eggeler, A. Ludwig (2010), *Identification of quaternary shape memory alloys with "zero" thermal hysteresis and unprecedented functional stability*, **Advanced Functional Materials**, 20, 1917 – 1923.

Understanding of the influence of alloying elements on phase stabilities in Ni- and Co-based superalloys in ternary model systems (TCP phases)

- high-temperature processing of materials libraries (> 1000°C)
- identification of compositions showing particular phases / or properties
- high-throughput oxidation studies

Cr-Ni-Re, Co-Ti-W, Ni-Al-Cr, Co-Al-W, …





Ar overpressure to lower sublimation of elements like Al, Mn at high temperatures

SFB/Transregio 103
SUPERALLOY SINGLE CRYSTALS

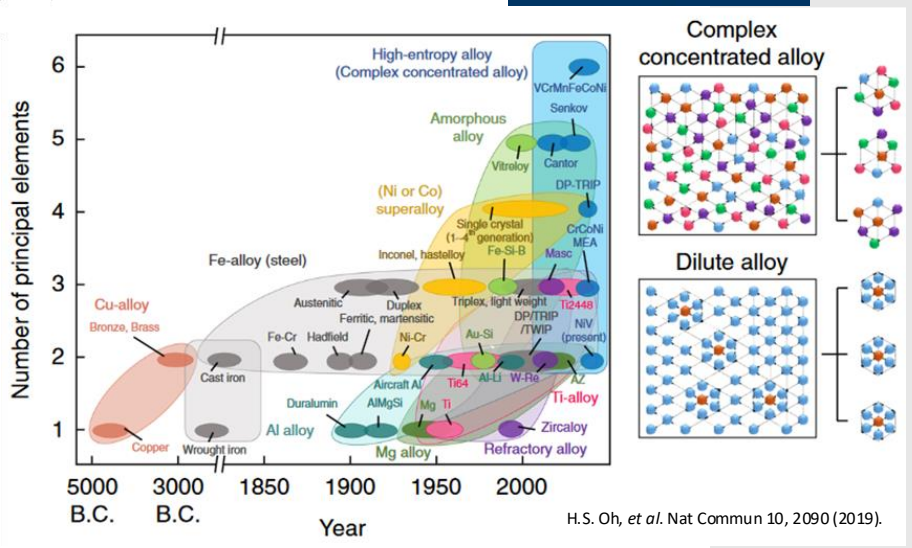
A. Janghorban, J. Pfetzing-Micklich, J. Frenzel, A. Ludwig (2014), *Investigation of the thin film system Cr-Ni-Re by high-throughput experimentation*, Advanced Engineering Materials, Vol. 16, 588-593

High entropy alloys

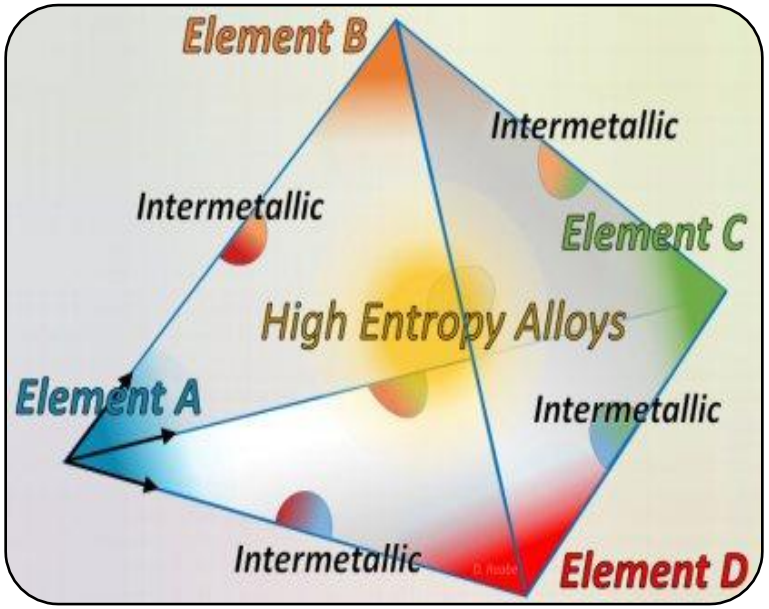
„Alloying has long been used to confer desirable properties to materials. Typically , it involves the addition of relatively small amounts of secondary elements to a primary element.“
e.g. Fe alloys, Al alloys,Ti alloys, Ni alloys and so on

new alloying strategy:
combination of multiple principal elements in high concentrations (often equiatomic) to create „high-entropy alloys“

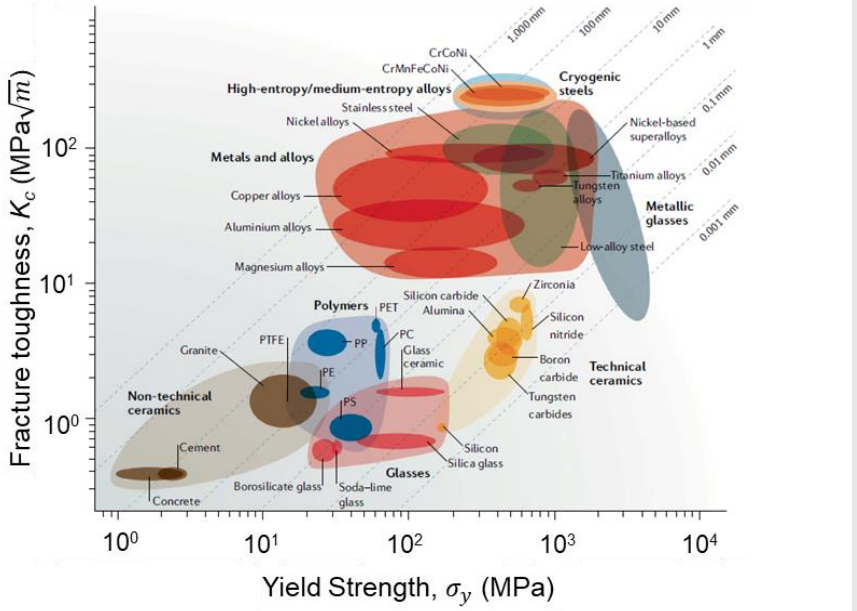
Large search space is offered,
some promising materials already discovered, many more expected



H.S. Oh, *et al.* Nat Commun 10, 2090 (2019).



https://www.dierk-raabe.com/high-entropy-alloys-overview/



George, Raabe, Ritchie, Nat Rev Mater 4, 515–534 (2019).
https://doi.org/10.1038/s41578-019-0121-4

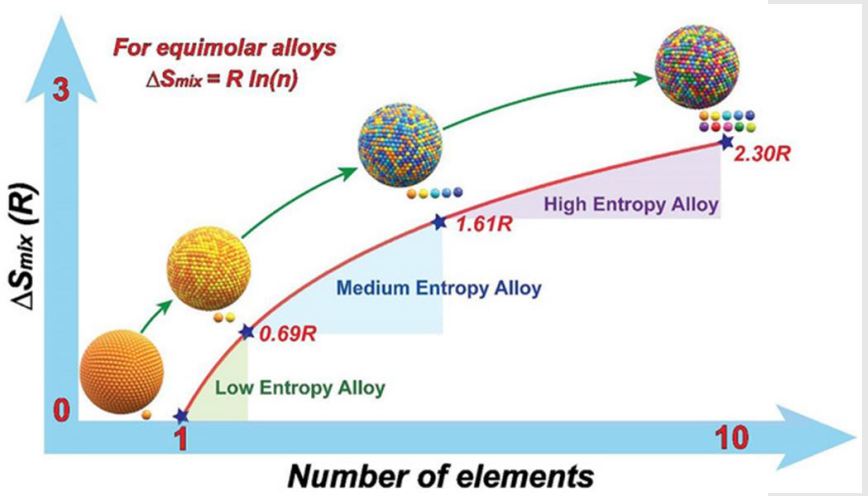
Multinary phases

High entropy alloys

J. W. Yeh et al. provided a rationale for HEAs:
they hypothesized that the presence of multiple (five or more) elements in near-equiatomic proportions would increase the configurational entropy of mixing by an amount sufficient to overcome the enthalpies of compound formation, thereby deterring the formation of potentially harmful intermetallics.

This was a counterintuitive notion because the conventional view — likely based on binary phase diagrams in which solid solutions are typically found at the ends and compounds near the centres — was that the greater the number of elements in concentrated alloys, the higher the probability that some of the elements would react to form compounds.
But Yeh et al. reasoned that, as the number of elements in an alloy increased, the entropic contribution to the total free energy would
overcome the enthalpic contribution and, thereby, stabilize solid solutions.

HEA: 5 or more elements in relatively high concentrations (5–35 at.%)



H. Liu, *et al.*, SusMat.,1:482–505 (2021).

Single-phase, solid-solution HEAs
with face-centred cubic (**fcc**), body-centred cubic (**bcc**),
hexagonal close- packed (hcp) and orthorhombic crystal structures have been identified.

Yeh, J. W. et al.
Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes.
Adv. Eng. Mater. 6, 299–303 (2004).

https://doi.org/10.1038/s41578-019-0121-4

Multinary phases

High entropy alloys

Box 1 | **Thermodynamics of phase stability**

An alloy created by combining two pure elements A and B can form a solid solution or one or more intermetallic phases, depending on the relative free energies of the following reactions:

$$A + B = AB\ (\text{solution}) : \Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (1)$$

$$A + B = AB\ (\text{intermetallic}) : \Delta G_{f} = \Delta H_{f} - T\Delta S_{f} \quad (2)$$

where ΔG_{mix}, ΔH_{mix} and ΔS_{mix} are the Gibbs free energy, enthalpy and entropy of mixing, respectively; ΔG_{f}, ΔH_{f} and ΔS_{f} are the corresponding values for the formation of an intermetallic compound with AB stoichiometry; and T is the absolute temperature. If, instead, two intermetallic compounds with different stoichiometries form (such as AB_2 or A_2B), additional expressions similar to Eq. 2 are needed for each compound.

At thermodynamic equilibrium, the phases present in the alloy depend on whether the Gibbs free energy of mixing (Eq. 1) is more or less negative than the free energies of formation (Eq. 2) of all possible intermetallic compounds comprising the elements A and B (that is, A_iB_j, where $i, j = 1, 2, 3, \ldots$) present individually or as mixtures. Note that it is not necessary for A + B to transform entirely into A_iB_j-type intermetallics; rather, intermetallics can precipitate within an A-rich or B-rich (terminal) solid solution, in which case the relevant free-energy change involves the sum of the free energy of mixing of the terminal solid solution and the free energy of formation of the intermetallic. Additionally, if intermetallic compounds are not favoured and only a solid solution forms, the solid solution need not be random (or ideal) because the different atomic species can cluster or order on the lattice, depending on whether ΔH_{mix} is positive or negative, respectively. Another possibility is that, instead of forming a single solid solution, the mixture decomposes into two solid solutions with different compositions, crystal structures and/or lattice parameters.

The situation becomes increasingly more complex as more alloying elements are added (A + B + C + …) because the number of possible phases that can co-exist correspondingly increases, as given by the Gibbs phase rule. If some of those phases are intermetallic compounds, they can be of several different types, even if we consider just the binary pairs (A–B, B–C, A–C, …). In reality, ternary and higher-order intermetallics, which need not all be line compounds, can also form, rapidly escalating the number of possibilities. In cases in which the compounds exhibit a compositional range of stability, the energies of the defects needed to accommodate deviations from stoichiometry (for example, anti-site defects) have to be accounted for. Some of the possible mixing reactions are shown in FIG. 1.

Even in simple A–B-type alloys, there is rarely complete miscibility across the entire composition range (from pure A to pure B). Rather, binary-phase diagrams typically exhibit solid solutions near the pure-element ends and a variety of intermetallic compounds in between, many of which are brittle. The problem is exacerbated in multi-element alloys, in which there are many more element pairs that can attract each other and, therefore, an increased number of potentially brittle intermetallics.

https://doi.org/10.1038/s41578-019-0121-4

Multinary phases

High entropy alloys

The traditional reluctance of metallurgists to work with concentrated, multi-element alloys was turned on its head by Yeh and co-workers[1], who proposed that the increased configurational entropy of mixing in alloys comprising multiple alloying elements (Eq. 1) would counteract the tendency for compound formation (Eq. 2). By adding more and more elements at near-equiatomic concentrations, it would be possible to stabilize solid solutions at the expense of intermetallics.

Yeh and co-workers[1] simplified the problem by assuming that the considered solid solution is ideal, in which case ΔH_{mix} in Eq. 1 is zero, and that the competing intermetallic compound is perfectly ordered, in which case ΔS_f in Eq. 2 is zero. The relative stabilities of the solid solution and intermetallic compound then depend on whether $-T\Delta S_{mix}$ (Eq. 1) is more negative than ΔH_f (Eq. 2). The ideal entropy of mixing is given by:

$$\Delta S_{mix} = -R\Sigma x_i \ln x_i \quad (3)$$

where R is the gas constant and x_i is the mole fraction of the i^{th} element. In an equiatomic alloy, $x_1 = x_2 = x_3$ and so on, and the mixing entropy becomes:

$$\Delta S_{mix} = R \ln n \quad (4)$$

where n is the number of elements in the alloy, yielding values for ΔS_{mix} of $1.39R$, $1.61R$ and $1.79R$ for equiatomic alloys containing 4, 5 and 6 elements, respectively.

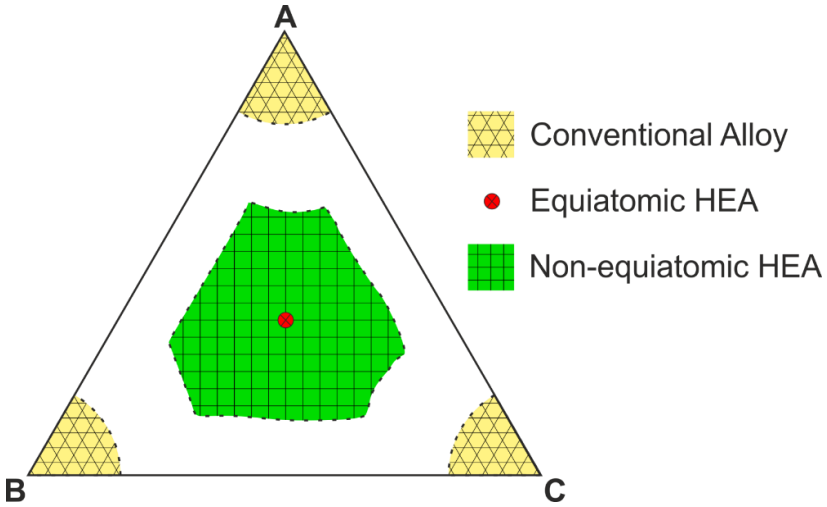
Based on this simplification, they concluded that, in alloys with a high number of principal elements (say, $n = 5$), the entropic contribution to the free energy ($-T_m\Delta S_{mix}$) at the melting temperature T_m is comparable to the formation enthalpies (ΔH_f) of strong intermetallic compounds such as NiAl and TiAl, thereby suppressing compound formation, except those with large heats of formation, such as strong ceramic compounds (oxides, carbides, nitrides and silicides), and more easily yielding random solid solutions during solidification. Consequently, Yeh and co-workers defined high-entropy alloys as those with five or more elements in equiatomic concentrations. To allow for flexibility in alloy design, they relaxed the equiatomic requirement and permitted a range of concentrations from 5 to 35 at.% for each constituent element. However, this simple criterion based on the number of alloying elements is not sufficient to predict single-phase, solid-solution formation in multi-element alloys.

https://doi.org/10.1038/s41578-019-0121-4

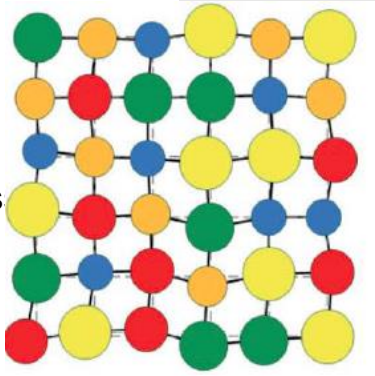
Multinary phases

HEA et al. …

High entropy alloys (HEAs),
High entropy materials (HEM), e.g. high entropy oxides (HEOs)
Complex concentrated alloys (CCAs)
Multiple principal element alloys (MPEAs)
Compositionally complex solid solutions (CCSS)



- **high entropy effect**:
  - High configurational entropy favor **solid solution phases** over competing intermetallics.
- **lattice distortion effect**:
  - Lattice distortions are more severe than in conventional alloys, and increase hardnes reduce electrical / thermal conductivity……
- **sluggish diffusion effect**:
  - Diffusion is sluggish in HEAs.
- **'cocktail' effect**:
  - The result of synergistic mixture is unpredictable and greater than the sum of the parts.



Z. Li, *et al.*, JOM, 69, 2099 (2017).

HEAs: Cantor alloy, CrMnFeCoNi

The CrMnFeCoNi alloy was one of the first equiatomic HEAs reported to crystallize as a single-phase fcc solid solution.

It was later discovered that it decomposes into metallic (bcc Cr) and intermetallic ($L1_0$-NiMn and B2-FeCo) phases below about 800°C.

HEAs: Senkov alloy, TiZrHfNbTa

bcc TiZrHfNbTa alloy.
Compared with extensive information available on the Cantor alloy and its derivatives, little is known about the fundamental structure–property relations in bcc HEAs, especially the refractory HEAs

Cantor, B., Chang, I. T. H., Knight, P. & Vincent, A. J. B. Microstructural development in equiatomic multicomponent alloys. Mater. Sci. Eng. A 375, 213–218 (2004).

Example for search of new HEAs

nature materials
LETTERS
https://doi.org/10.1038/s41563-020-0750-4
Check for updates

Natural-mixing guided design of refractory high-entropy alloys with as-cast tensile ductility

Shaolou Wei[1], Sang Jun Kim[2], Jiyun Kang[1], Yong Zhang[3], Yongjie Zhang[4], Tadashi Furuhara[4], Eun Soo Park[2] and Cemal Cem Tasan[1]✉

Metallic alloys containing multiple principal alloying elements have created a growing interest in exploring the property limits of metals and understanding the underlying physical mechanisms. Refractory high-entropy alloys have drawn particular attention due to their high melting points and excellent softening resistance, which are the two key requirements for high-temperature applications. Their compositional space is immense even after considering cost and recyclability restrictions, providing abundant design opportunities. However, refractory high-entropy alloys often exhibit apparent brittleness and oxidation susceptibility, which remain important challenges for their processing and application. Here, utilizing natural-mixing characteristics among refractory elements, we designed a $Ti_{38}V_{15}Nb_{23}Hf_{24}$ refractory high-entropy alloy that exhibits >20% tensile ductility in the as-cast state, and physicochemical stability at high temperatures. Exploring the underlying deformation mechanisms across multiple length scales, we observe that a rare β′-phase plays an intriguing role in the mechanical response of this alloy. These results reveal the effectiveness of natural-mixing tendencies in expediting high-entropy alloy discovery.

The quick-emerging paradigm of metallic alloy development with multiple principal elements has rendered salient advantages Moreover, because of their apparent brittleness below homologous temperatures[21], fundamental investigations of the deformation mechanisms of RHEAs are scant, especially compared to the abundant literature for face-centred cubic (fcc)-structured high-entropy alloys (HEAs)[22,23]. We reveal in this work that by following a Cantor-like approach[1] that exploits the natural-mixing characteristics among refractory elements to minimize casting segregation, it is possible to expediently guide the RHEA composition search, and thereby to achieve desirable combinations of strength, ductility and high-temperature stability.

The first step of our composition-searching strategy involves quantitative elemental partition assessment at the mesoscale, by probing the largest single-phase region inherited from natural mixing among refractory elements. To achieve this, a nine-component master RHEA consisting of equal atomic portions of Ti, V, Cr, Zr, Nb, Mo, Hf, Ta and W was cast via arc melting. As displayed in Fig. 1a, four predominant phase-separated zones develop in this master RHEA's microstructure, respectively enriched in Ti, Mo, Cr and Hf (see the markers as a guide in Fig. 1a). Applying energy dispersive spectroscopy (EDS) elemental mapping and point analyses to the largest single-phase region that spans over almost the full microstructure, and considering alloying elements >10 at.% as principal constituents (for more details, see Supplementary Note 1), we

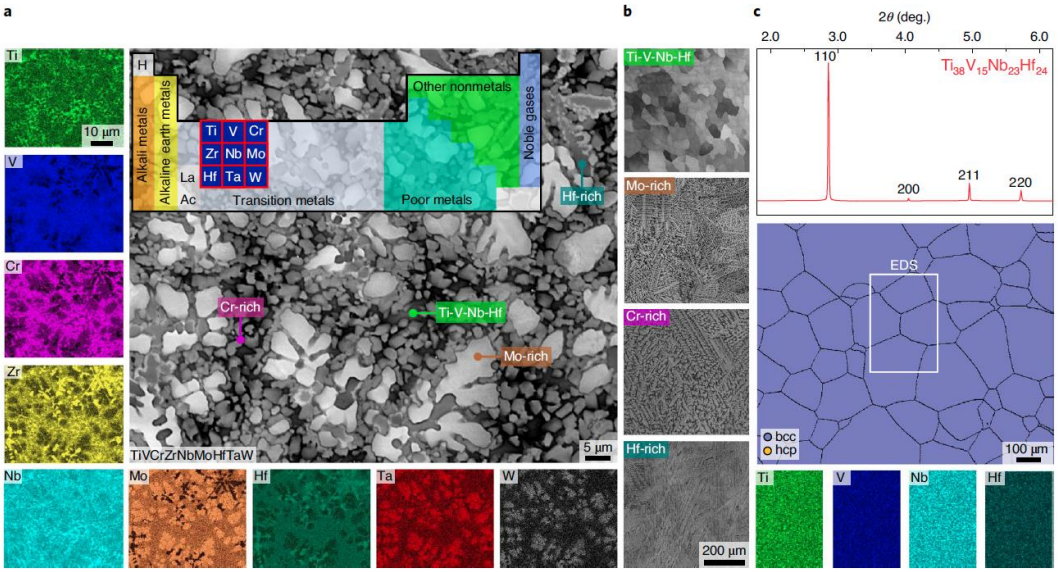


Fig. 1 | The strategy of composition search among refractory elements. a, As-cast microstructure of a master RHEA consisting of the nine refractory elements in equal atomic portions. The corresponding EDS mapping results reveal the distinctive presence of four phase-separated regions, respectively enriched in Ti, Mo, Cr and Hf. **b**, As-cast microstructures of the four alloys designed using the compositions excerpted from the corresponding regions in **a** (more details are provided in Supplementary Fig. 1, Supplementary Table 1 and Supplementary Note 1). **c**, Microstructural characterization of the recrystallized $Ti_{38}V_{15}Nb_{23}Hf_{24}$ RHEA whose composition was inherited from the largest single-phase region in **a** (denoted Ti-V-Nb-Hf). In Supplementary Note 1, we provide systematic assessments of the reliability for the approach and discuss the plausible thermodynamic principles in terms of universality. Sub-figures presented from top to bottom in **c** are synchrotron X-ray diffraction patterns, EBSD phase map and EDS elemental distribution assessment of a selected area of interest (the white rectangle in the phase map). Magnifications of EBSD and EDS are identical. All the mesoscale characterizations indicate that the $Ti_{38}V_{15}Nb_{23}Hf_{24}$ RHEA preserves a single-phase bcc structure, macroscopically, with a lattice parameter $a = 3.323$ Å.

High entropy materials (oxides, nitrides, …)

REVIEWS

Check for updates

High-entropy ceramics

Corey Oses[1,2], *Cormac Toher*[1,2] *and Stefano Curtarolo*[1,2]✉

Abstract | Disordered multicomponent systems, occupying the mostly uncharted centres of phase diagrams, were proposed in 2004 as innovative materials with promising applications. The idea was to maximize the configurational entropy to stabilize (near) equimolar mixtures and achieve more robust systems, which became known as high-entropy materials. Initial research focused mainly on metal alloys and nitride films. In 2015, entropy stabilization was demonstrated in a mixture of oxides. Other high-entropy disordered ceramics rapidly followed, stimulating the addition of more components to obtain materials expressing a blend of properties, often highly enhanced. The systems were soon proven to be useful in wide-ranging technologies, including thermal barrier coatings, thermoelectrics, catalysts, batteries and wear-resistant and corrosion-resistant coatings. In this Review, we discuss the current state of the disordered ceramics field by examining the applications and the high-entropy features fuelling them, covering both theoretical predictions and experimental results. The influence of entropy is unavoidable and can no longer be ignored. In the space of ceramics, it leads to new materials that, both as bulk and thin films, will play important roles in technology in the decades to come.

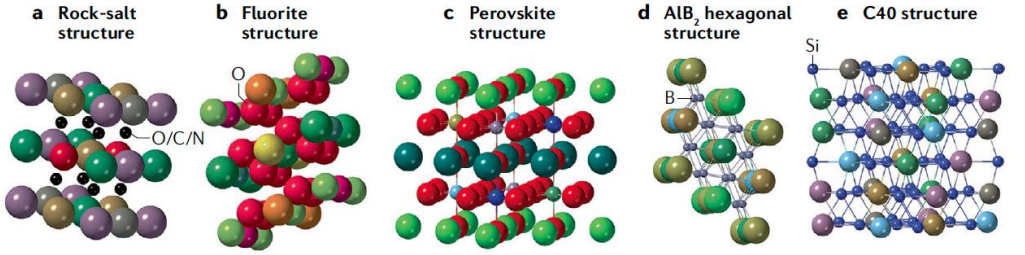


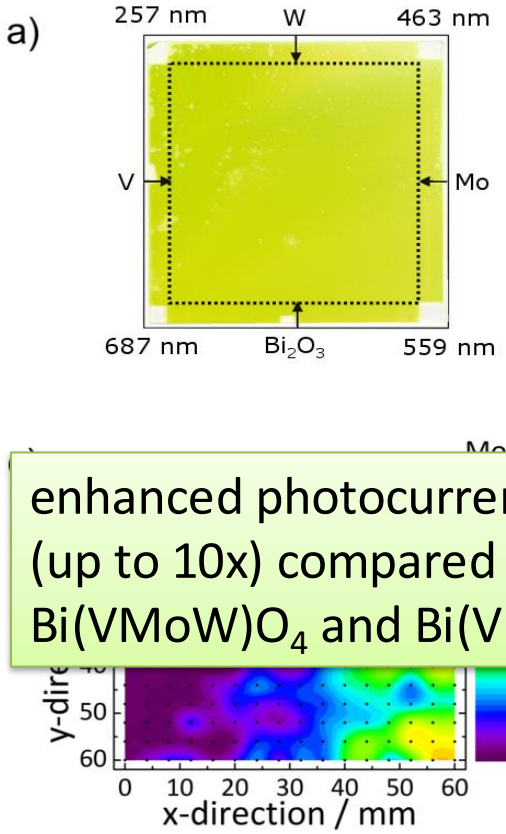
Fig. 2 | **High-symmetry structures of high-entropy ceramics.** Structures and compositions include the rock-salt structure (space group $Fm\bar{3}m$ #225, AFLOW (Automatic Flow Framework for Materials Science)[93] prototype label[94,95] AB_cF8_225_a_b) (oxides, carbides, nitrides) (part **a**), the fluorite structure ($Fm\bar{3}m$ #225, AB2_cF12_225_a_c) (oxides) (part **b**), the perovskite structure ($Pm\bar{3}m$ #221, AB3C_cP5_221_a_c_b) (oxides) (part **c**), the AlB_2 hexagonal structure ($P6/mmm$ #191, AB2_hP3_191_a_d) (borides) (part **d**) and the C40 structure ($P6_222$ #180, AB2_hP9_180_d_j) (silicides) (part **e**).

www.nature.com/articles/s41578-019-0170-8

compositionally complex ceramics
high entropy metal sublattice ceramics

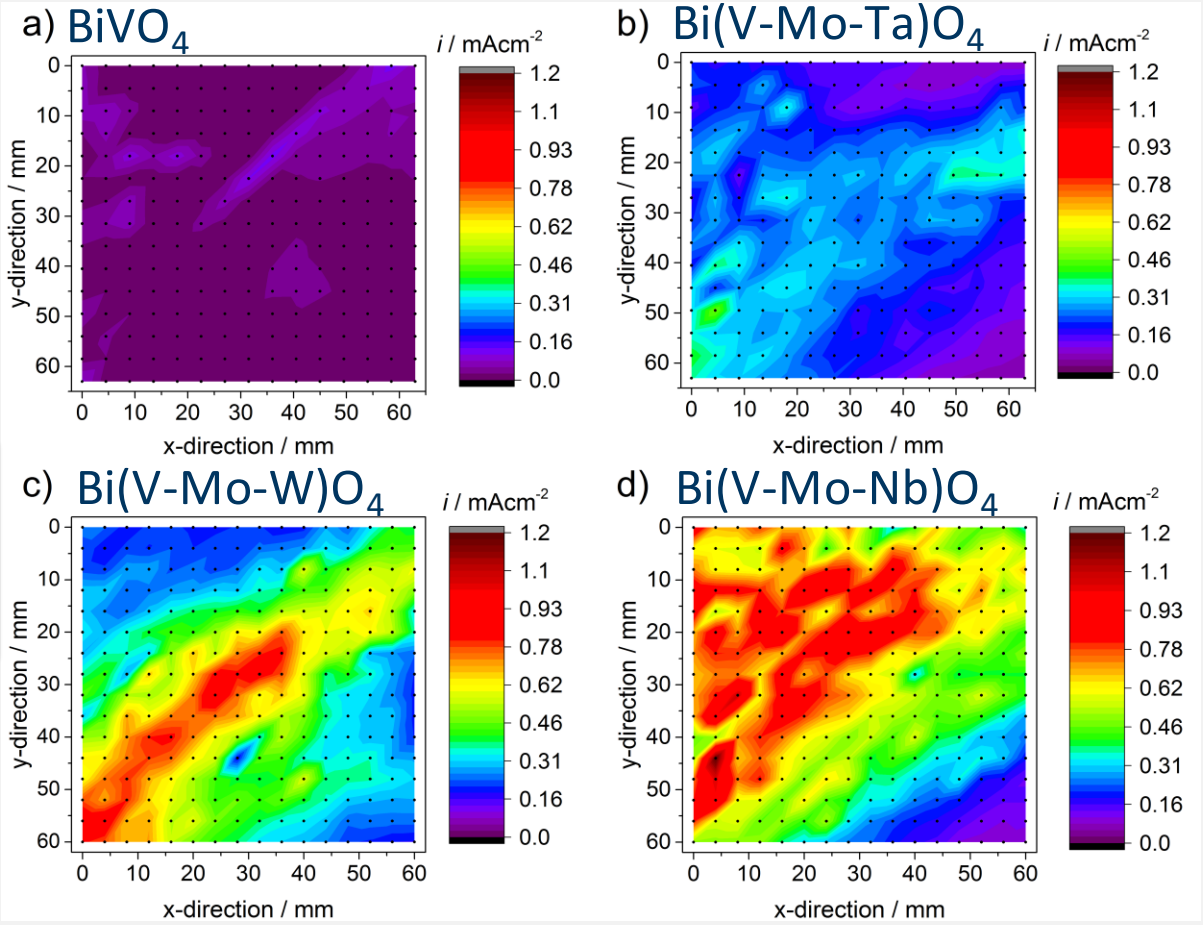
J. Appl. Phys. 130, 150903 (2021); doi: 10.1063/5.0062523

Compositional effects on solar water splitting in $Bi(V\text{-}Mo\text{-}X)O_4$, X: Ta, W, Nb



enhanced photocurrents
(up to 10x) compared to $BiVO_4$ in $Bi(VMoW)O_4$ and $Bi(VMoNb)O_4$

Photoelectrochemistry 1.23 V vs. RHE (0.1 M borate buffer, pH = 9)



R. Gutkowski, C. Khare, F. Conzuelo, Y.U. Kayran, A. Ludwig, W. Schuhmann (2017)
Unraveling compositional effects on the light-induced oxygen evolution in $Bi(V\text{-}Mo\text{-}X)O_4$ material libraries,
Energy & Environmental Science

Multinary phases

High entropy nanomaterials

RESEARCH | REVIEW

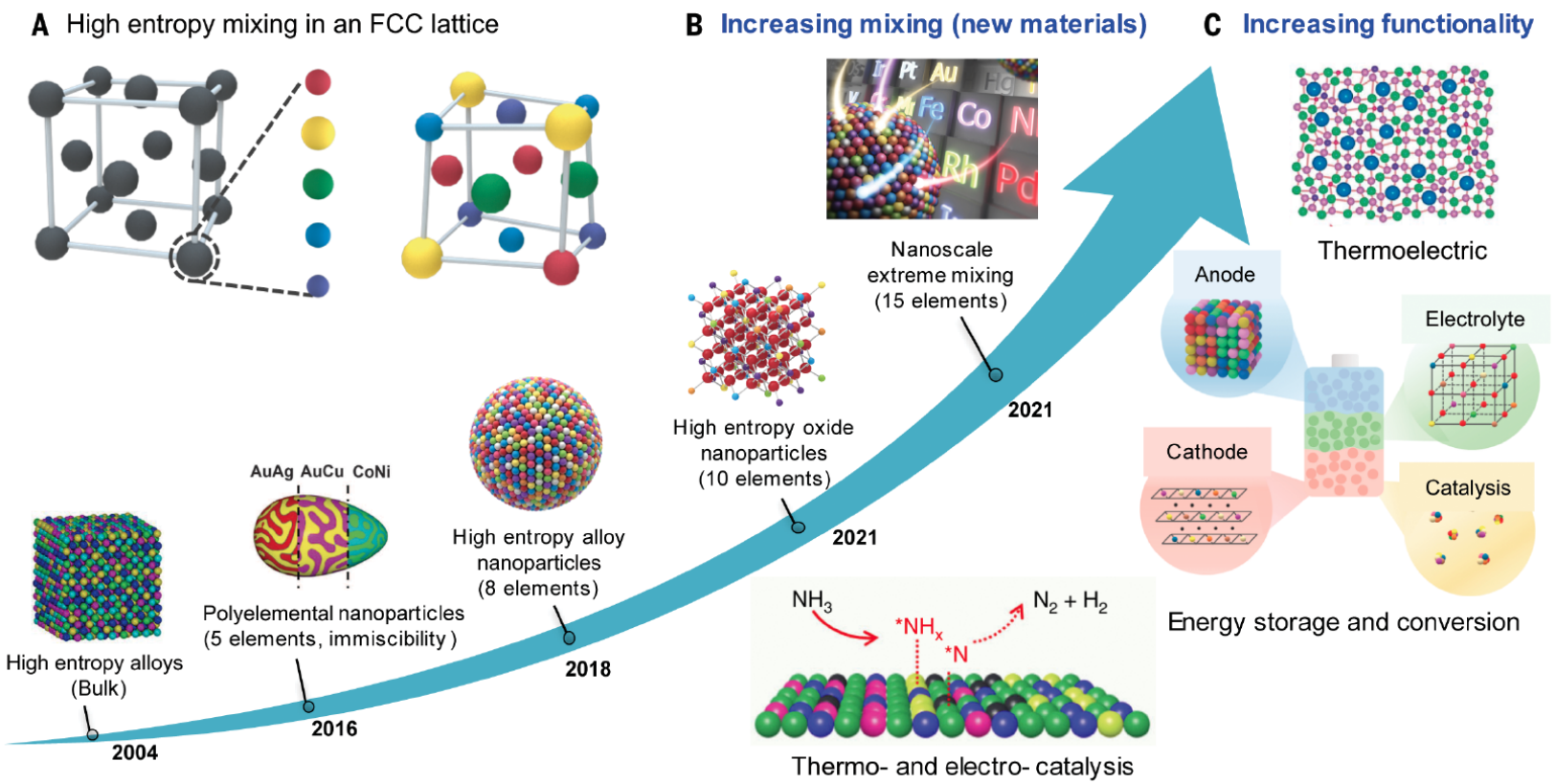


Fig. 1. Development of high-entropy nanoparticles with multielemental composition and enhanced functionality. (**A**) Schematic showing high-entropy mixing in a face-centered cubic lattice. Multiple elements will occupy the same lattice site randomly to form a high-entropy structure such as a high-entropy alloy. (**B**) The study of bulk high-entropy alloys has taken off and gained substantial interests since 2004 (*1*, *3*). In 2016, a multielemental nanoparticle library was synthesized (though with immiscibility, and thus phase segregation), followed by various single-phase, high-entropy nanoparticles with an increasing number and range of elements (*7*, *8*, *14*, *20*). Reprinted from (*14*) with permission from Elsevier. (**C**) These high-entropy nanoparticles have found critical application in thermo- and electro-catalysis, energy storage and conversation, and environmental and thermoelectric technologies (*29*–*31*, *35*, *36*). Reprinted from (*31*) with permission (copyright 2021 American Chemical Society) and from (*35*) with permission. Other portions of the figure are reprinted from (*7*, *8*) with permission, from (*20*) with permission from Springer-Nature, and from (*36*) CC BY 4.0.

Yao et al., High-entropy nanoparticles: Synthesis-structure property relationships and data-driven discovery, Science 376, eabn3103 (2022), https://doi.org/10.1126/science.abn3103

High entropy nanomaterials

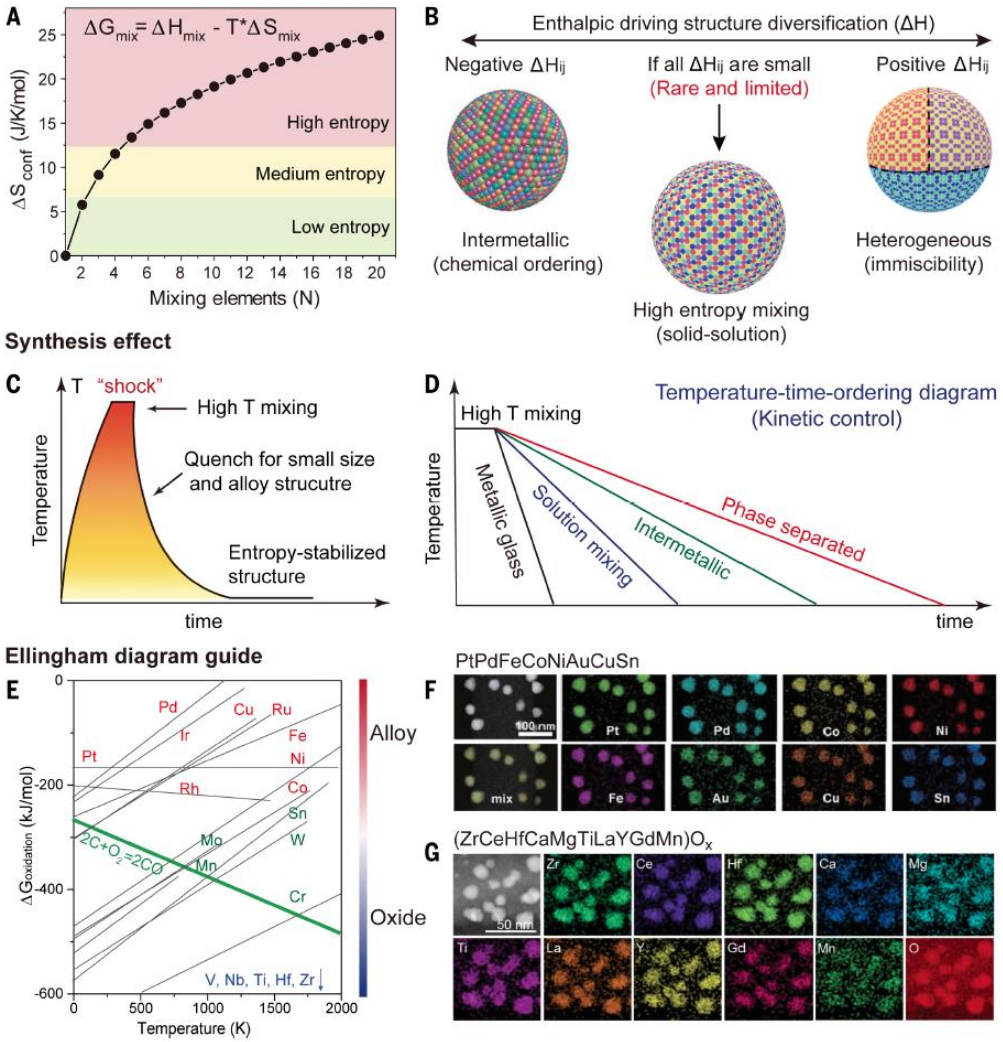


Fig. 2. High-entropy nanoparticle synthesis and structure. Thermodynamic analysis of high-entropy mixing considers both entropy (**A**) and enthalpy (**B**), which are mainly determined by the composition of high-entropy nanoparticles (*8*). (**C**) Thermal shock synthesis of high-entropy nanoparticles features a high-temperature pulse for elemental mixing and then rapid temperature quenching to maintain the high-entropy structure. (**D**) Temperature-time-transformation diagram describing how the cooling rates of high-temperature, kinetically controlled syntheses can be adjusted to form various nanoparticles featuring different degrees of structural and chemical ordering. (**E**) The Ellingham diagram [reprinted from (*14*) with permission from Elsevier] provides a guide for composing either alloy (e.g., PtPdFeCoNiAuCuSn) (*8*) (**F**) or oxide high-entropy nanoparticles (e.g., ZeCeHfCaMgTiLaYGdMnO$_x$) (*20*) (**G**) according to the oxidation potentials of each element. Reprinted from (*20*) with permission from Springer Nature.

Yao et al., High-entropy nanoparticles: Synthesis-structure property relationships and data-driven discovery, Science 376, eabn3103 (2022). https://doi.org/10.1126/science.abn3103

Multinary phases

Mixing non-mixable elements in high entropy nanomaterials

Matter

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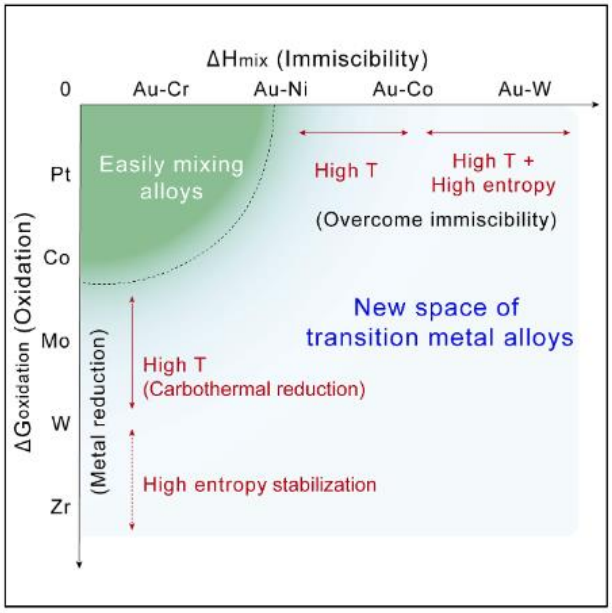
Article

Extreme mixing in nanoscale transition metal alloys



Conventionally, alloys are mostly synthesized in the region of easy mixing, i.e., with light immiscibility and oxidation potentials. Yet such a limited elemental combination largely hinders possible tunability and material discovery. By using entropic design (high temperature and high entropy) that favors uniform mixing, we extended nanoscale alloying to previous unmixable regions by including strongly immiscible and easily oxidized combinations, which we called an extreme mixing. The new alloy space could bring forth exotic nanomaterials for broad applications.

Yonggang Yao, Zhennan Huang, Lauren A. Hughes, ..., Andrew M. Minor, Reza Shahbazian-Yassar, Liangbing Hu

binghu@umd.edu

Highlights

A record 15-element nanoalloy was achieved by extreme entropic design and stabilization

Nanoscale alloys entered into regions featuring strong immiscibility and easy oxidation

Mixing enthalpy and Ellingham diagram can effectively guide the nanoscale alloy design

The first observation of localized strain and lattice distortions in extreme nanoalloys

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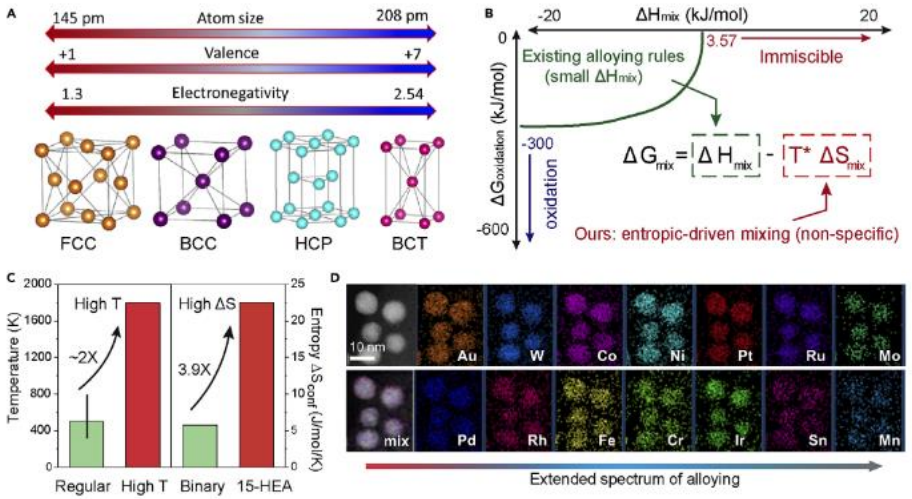

Figure 1. Extreme alloying by a high-temperature and high-entropy synthesis

(A) Transition metal elements and their largely different physiochemical properties.

(B) Existing single-phase alloying rule (a small ΔH_{mix}) and our strategies based on the entropic contribution ($-T\Delta S_{mix}$) to enable more alloy choices.

(C) The high temperature and high entropy (configurational entropy) in this study (1,800 K, 15 element mixing) compared with typical nanomaterial studies (300–800 K, binary systems), rendering an entropic driving force of approximately −40 kJ/mol.

(D) STEM elemental maps of extreme mixing in nanoparticles containing 15 different elements including both late and early transition metals, made possible by the high-temperature and high-entropy synthesis (Cu mapping data is not shown due to use of the Cu grid).

Multinary phases

Mixing non-mixable elements in high entropy nanomaterials

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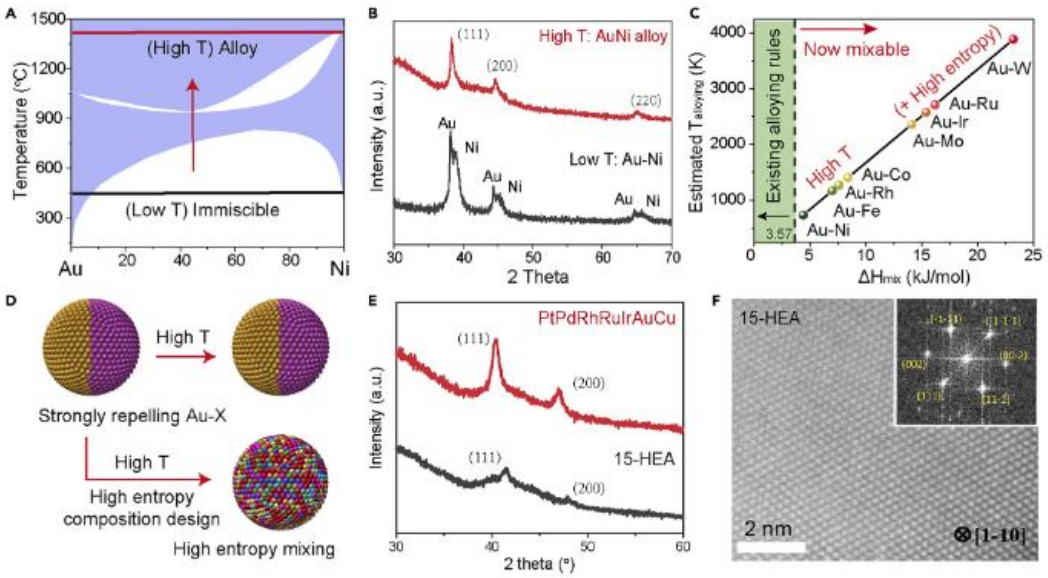


Figure 2. Overcoming immiscibility by high-temperature and high-entropy synthesis

(A) Phase diagram of Au-Ni, showing the immiscible region at low temperature.

(B) XRD profiles of Au-Ni synthesized by high-temperature shock (1,800 K, a single-phase structure) and low-temperature shock (800 K, phase separation of Au and Ni).

(C) Summary of general alloying in Au-based binary combinations. The high-temperature synthesis extends the alloying of elements up to Au-Co, while further extension requires a high-entropy compositional design. The alloying temperature is estimated from $T_{alloying} = \Delta H_{mix}/\Delta S_{mix}$.

(D) Schematic demonstrating the mixing of strongly repelling Au-X combinations with a high-entropy design.

(E) XRD profiles of a 7-element system of noble transition metals and a 15-HEA formulation; both samples show a single-phase structure despite containing strongly repelling combinations.

(F) Atomic-resolution HAADF image of a 15-HEA nanoparticle showing an FCC pattern (inset).

(G) Low-magnification element maps for 15-HEA nanoparticles, showing uniform mixing of early and late transition metals.

CellPress

Previews

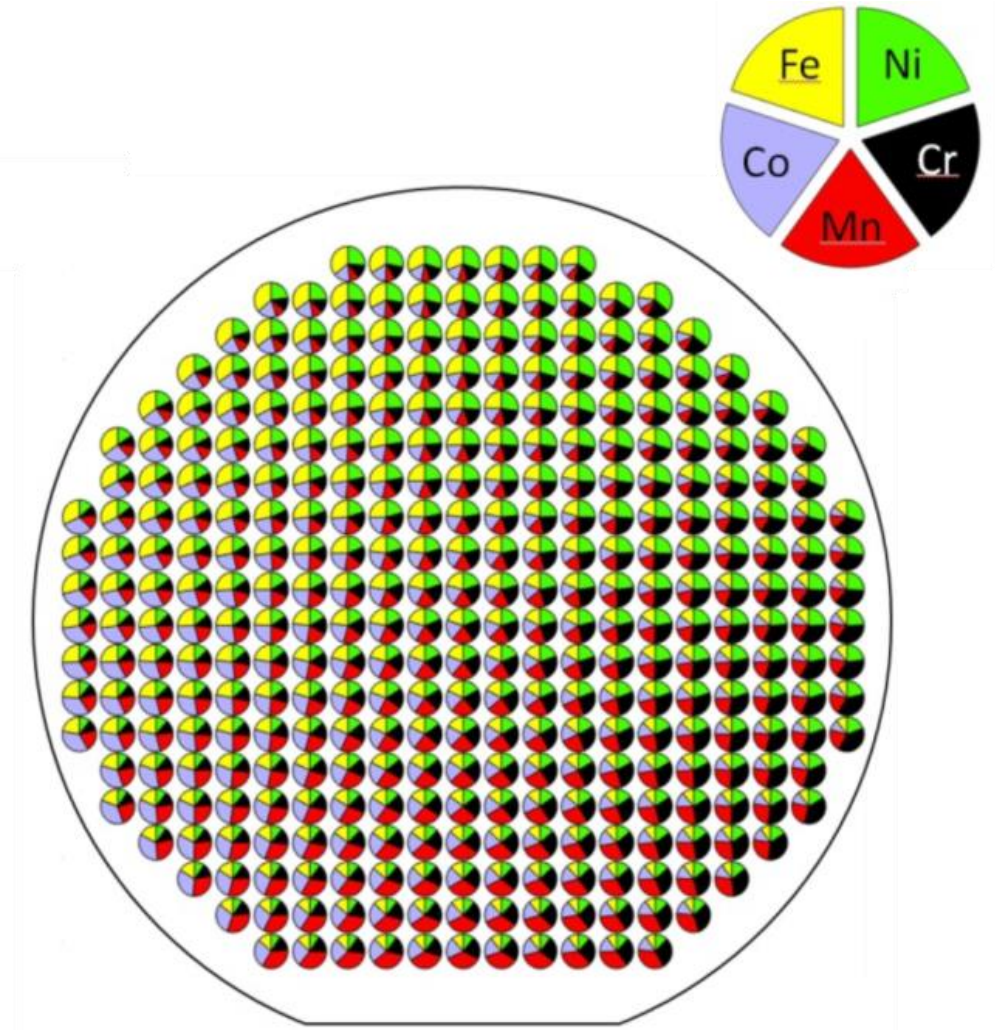
Maximize mixing in highly polyelemental solid solution alloy nanoparticles

Alfred Ludwig[1,*]

In this issue of *Matter*, Yao et al. report on advanced non-equilibrium high-temperature entropy-controlled synthesis of polyelemental nanoparticles. They achieve extreme mixing of 15 metals, some of them previously immiscible, in the form of a single phase solid solution. The compositionally tunable properties of such atomic scale mixtures within a simple crystal structure makes them highly interesting for the design of new materials, e.g., electrocatalysts.

https://doi.org/10.1016/j.matt.2021.06.015

Exploring quinary composition space: „high entropy“ alloys, multiple principal element alloys

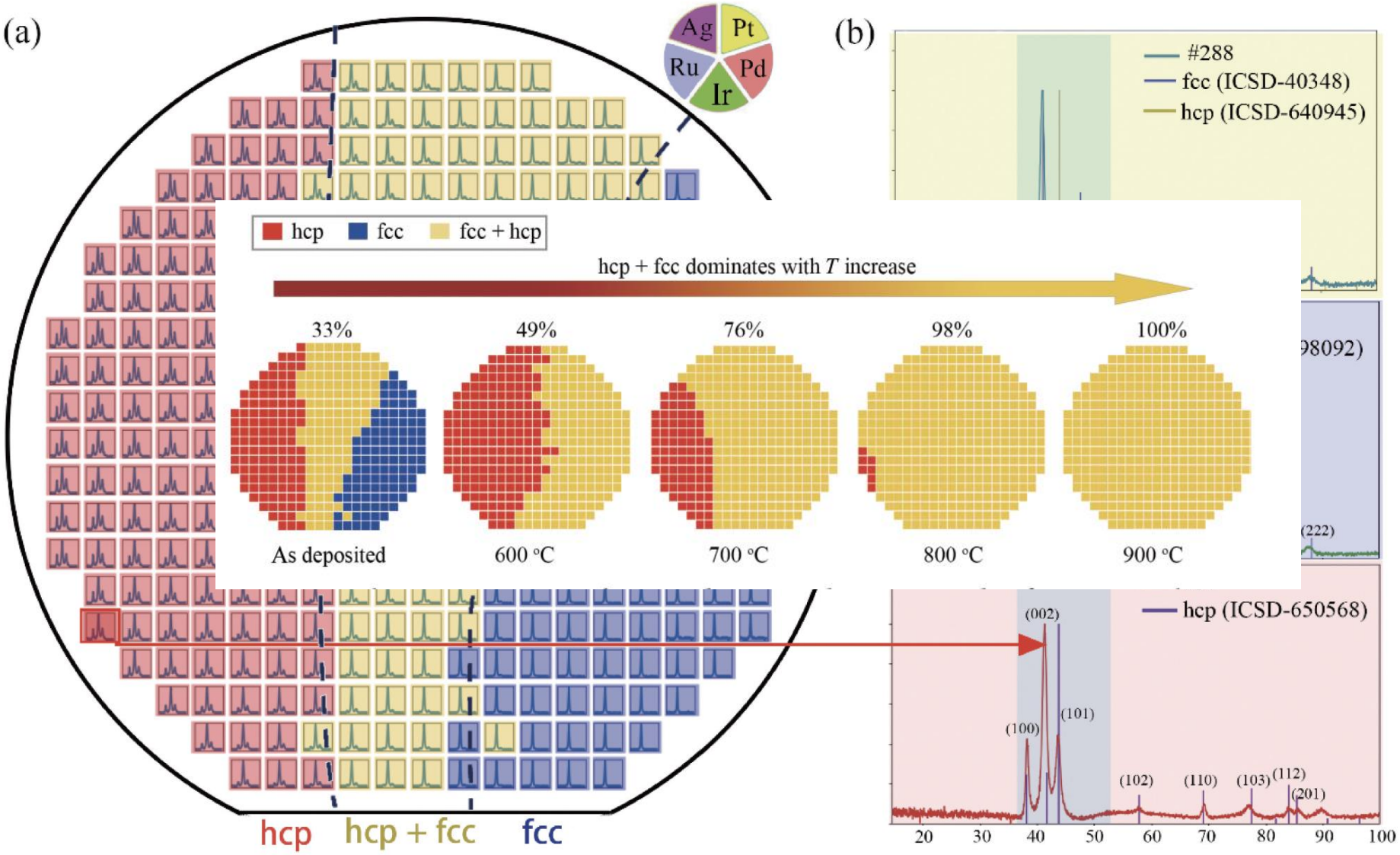


Visualization of multidimensional data

Co-sputter deposition of multinary materials libraries from up to 5 elemental targets

Z. Li, A. Ludwig, A. Savan, H. Springer, D. Raabe (2018) *Combinatorial metallurgical synthesis and processing of high-entropy alloys*, accepted by Journal of Materials Research

High-throughput characterization of materials libraries: Composition and phase constitution of a quinary system



B. Xiao, A. Savan, X. Wang, A. Ludwig (2021) *Phase constitution of the noble metal thin-film complex solid solution system Ag-Ir-Pd-Pt-Ru in dependence of elemental compositions and annealing temperatures*, Nano Research, https://doi.org/10.1007/s12274-021-3516-7

Materials informatics for XRD phase analysis: Towards autonomous experimentation

RUB

nature computational science

RESOURCE

https://doi.org/10.1038/s43588-021-00059-2

Check for updates

Crystallography companion agent for high-throughput materials discovery

Phillip M. Maffettone[1,2]✉, Lars Banko[3], Peng Cui[2], Yury Lysogorskiy[4], Marc A. Little[2], Daniel Olds[1], Alfred Ludwig[3] and Andrew I. Cooper[2]✉

The discovery of new structural and functional materials is driven by phase identification, often using X-ray diffraction (XRD). Automation has accelerated the rate of XRD measurements, greatly outpacing XRD analysis techniques that remain manual, time-consuming, error-prone and impossible to scale. With the advent of autonomous robotic scientists or self-driving laboratories, contemporary techniques prohibit the integration of XRD. Here, we describe a computer program for the autonomous characterization of XRD data, driven by artificial intelligence (AI), for the discovery of new materials. Starting from structural databases, we train an ensemble model using a physically accurate synthetic dataset, which outputs probabilistic classifications—rather than absolutes—to overcome the overconfidence in traditional neural networks. This AI agent behaves as a companion to the researcher, improving accuracy and offering substantial time savings. It is demonstrated on a diverse set of organic and inorganic materials characterization challenges. This method is directly applicable to inverse design approaches and robotic discovery systems, and can be immediately considered for other forms of characterization such as spectroscopy and the pair distribution function.

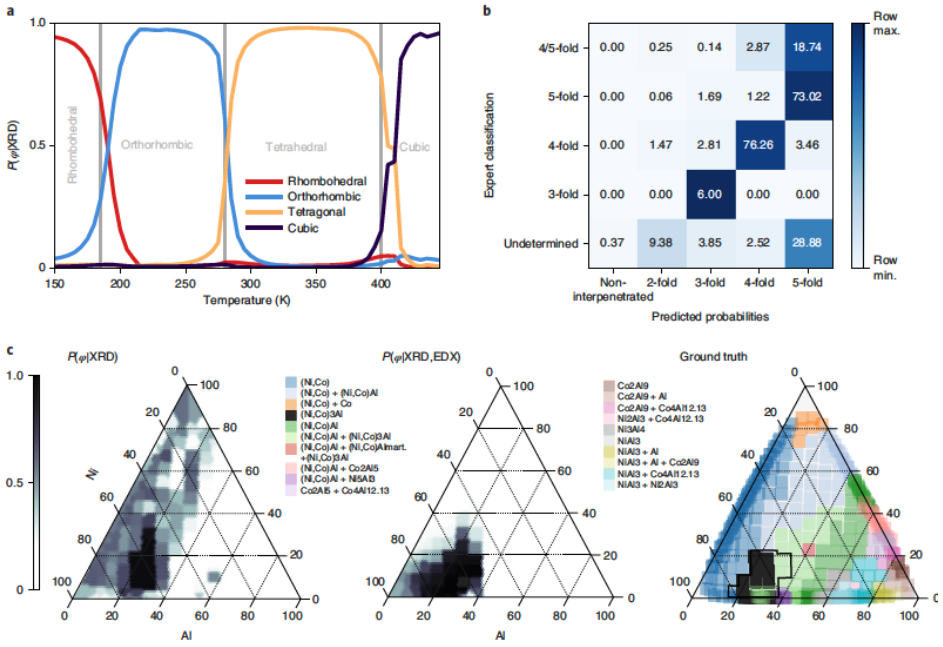


Fig. 4 | Autonomous XRD analysis results from XCA. a, XCA rapidly produces a probabilistic temperature-dependent phase mapping of $BaTiO_3$ that is more accurate than current refinement techniques. Dotted lines show the expected transition temperatures, and each colored line corresponds to the probability of a given phase existing. **b**, Confusion matrix showing the sum of predicted phase probabilities for each expert-classified phase of ADTA. **c**, Phase mapping for cubic Ni_3Al compared with the ground truth phase diagram, with a black line outlining the probability region of $P(\varphi_i|XRD, EDX) \geq 0.8$ (right). The XRD-based probability (left) captures the uncertainty associated with classifying this phase against another cubic phase with similar peak positions. The joint probability (center) reduces the uncertainty by conflating prior information from composition. Each of these results was produced by a single XCA experiment using 100,000 synthetic patterns per phase, and an ensemble of 50 CNN learners.

XCA: autonomous companion agent that learns from fully synthetic data and can predict phases from XRD patterns in real time

for the rapid, accurate classification of XRD datasets
effective across materials domains, requires no labeling of experimental data, and is robust despite varying degrees of texture, peak shifting, peak broadening, phase mixing and amorphous disorder

RESOURCE NATURE COMPUTATIONAL SCIENCE

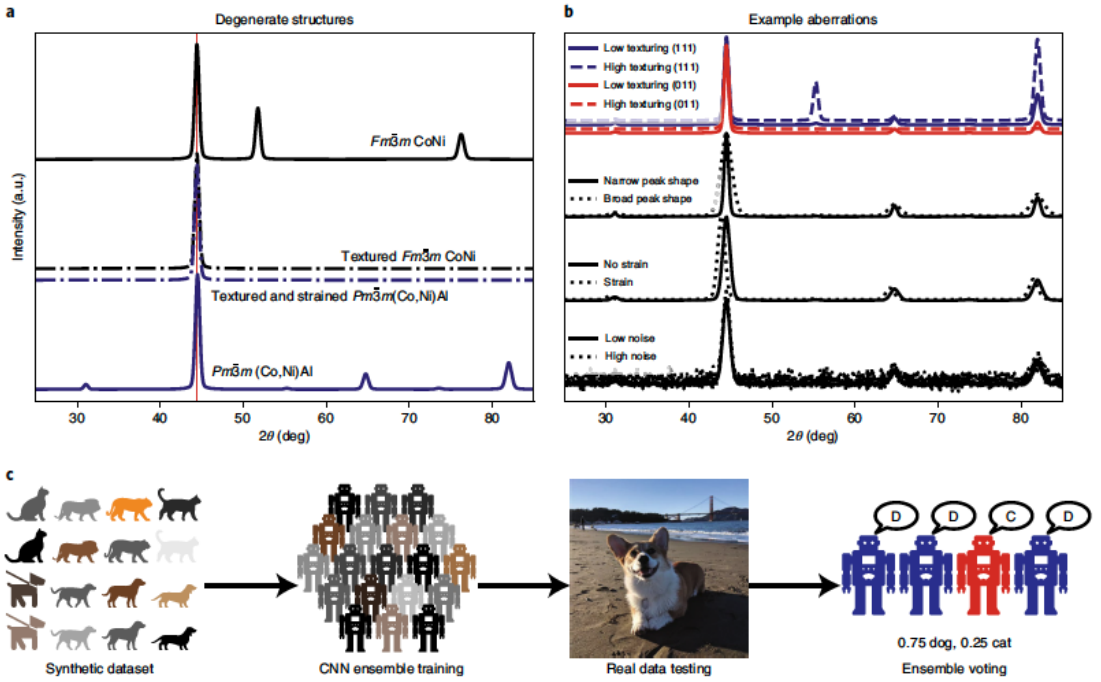
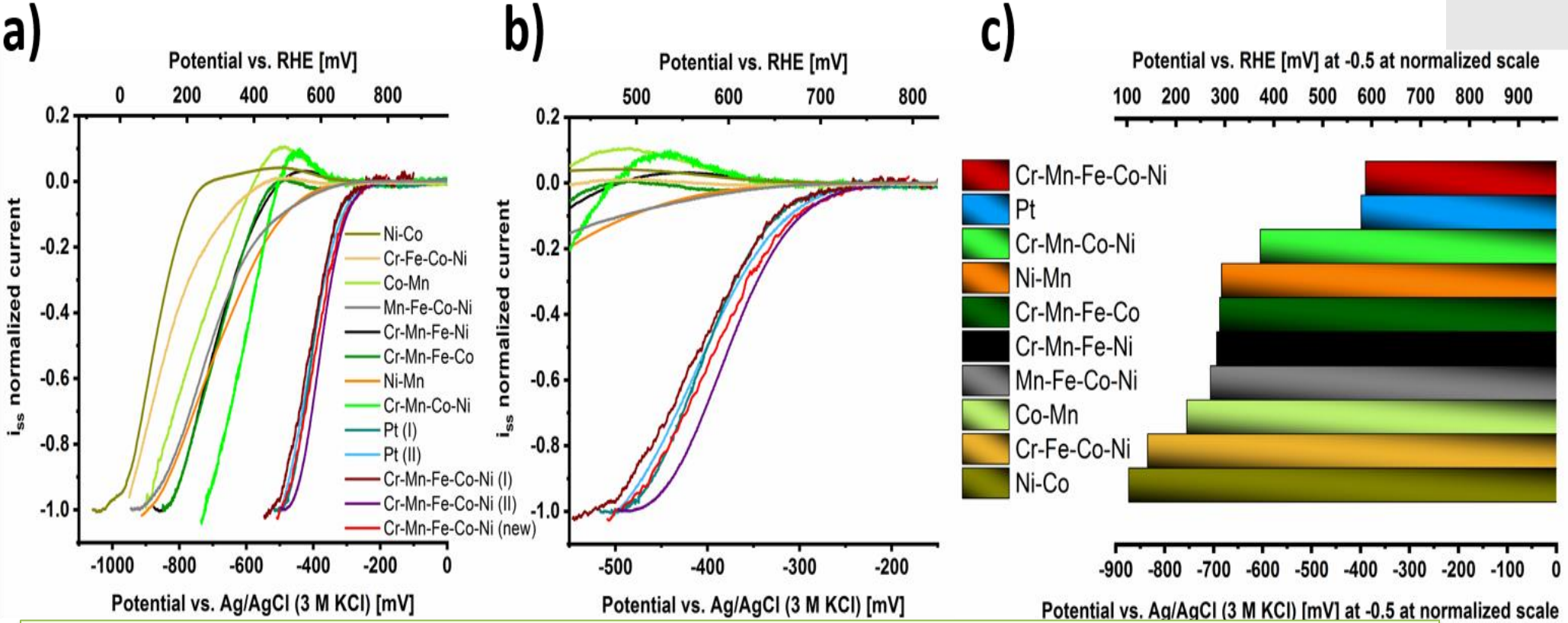


Fig. 1 | Experimental XRD complexity and training an ensemble using synthetic data. a, Different crystal phases can create identical XRD patterns under conditions that are common in thin-film experiments. **b**, There are many causes of aberration in an XRD pattern, such as intensity changes from the preferred orientation, peak shifting from lattice strain or solid solutions, peak broadening and background, as illustrated here for the $Pm\bar{3}m$ phase of (Ni,Co)Al. **c**, The crystallography companion agent (XCA) statistically solves the problem of simultaneous experimental complexity and data scarcity by automatically building a synthetic dataset and training an ensemble of learners from the data. The dataset covers the scope of variation in XRD patterns and the ensemble model outputs an existence probability of each phase when tested against real data. This protocol is analogous to training a cat-versus-dog classifier on artistic sketches of the animals and testing on photographs. Un like the sketch analogy, this training approach is possible for XRD because of the speed and accuracy of the simulations.

P. M. Maffettone, L. Banko, P. Cui, Y. Lysogorskiy, M. Little, D. Olds, A. Ludwig, A. I. Cooper (2021) *Crystallography companion agent for high-throughput materials discovery*. Nature Computational Science 1, 290 – 297.

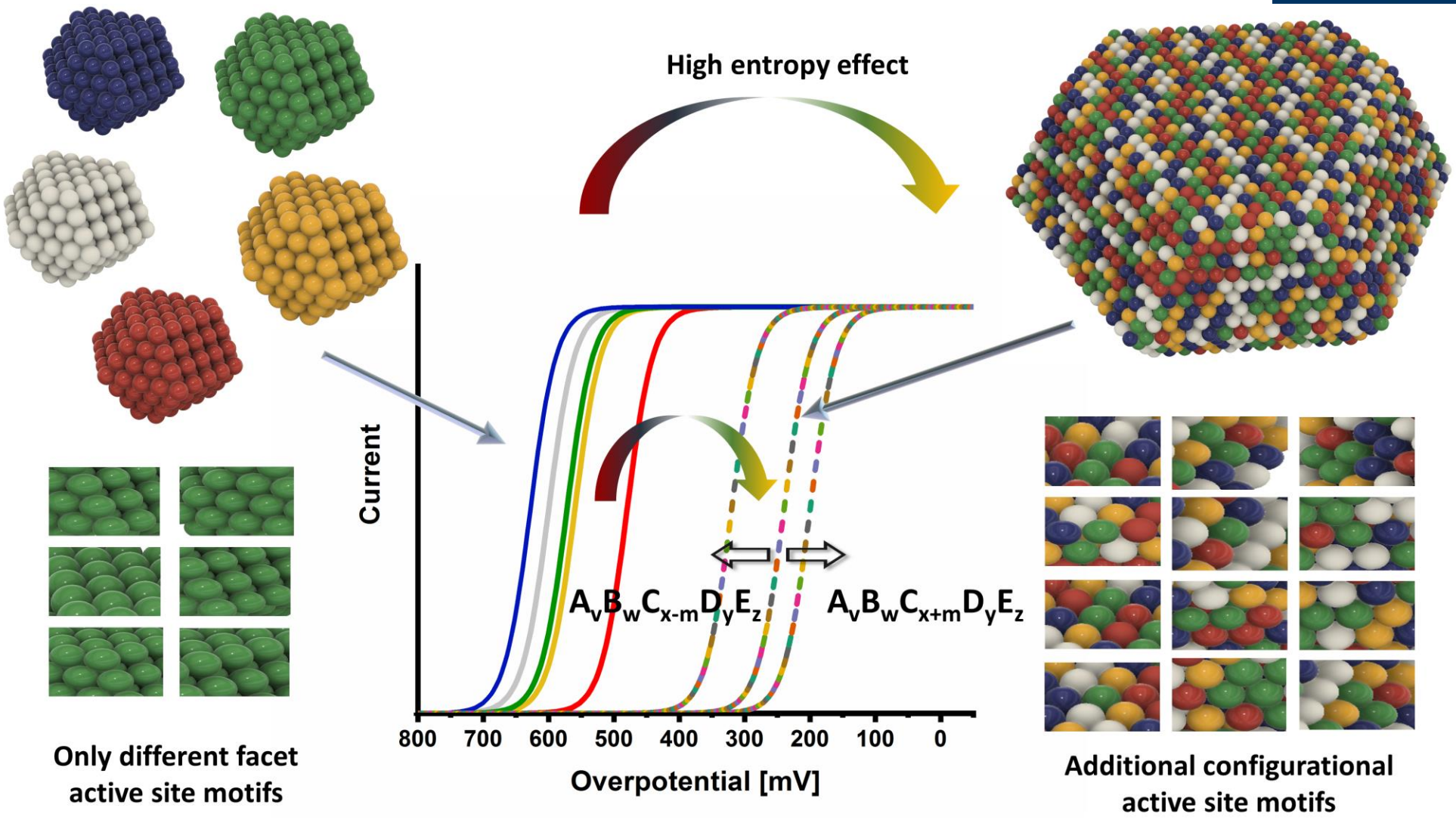
„High entropy“ alloy nanoparticle libraries: Cr-Mn-Fe-Co-Ni



Systematic removal of each element from the quinary system yields a significant drop in activity for all quaternary alloys, indicating the **importance of the synergistic combination of all 5 elements**, likely due to formation of a **single solid solution** phase with altered properties which enables overcoming limitations of single elements

T. Löffler, H. Meyer, A. Savan, P. Wilde, A. Garzón Manjón, Y.-T. Chen, E. Ventosa, C. Scheu, A. Ludwig, W. Schuhmann (2018) Discovery of a Multinary Noble Metal Free Oxygen Reduction Catalyst, Advanced Energy Materials1 802269

Cr-Mn-Fe-Co-Ni nanoparticle libraries: ORR catalysts



T. Löffler, H. Meyer, A. Savan, P. Wilde, A. Garzón Manjón, Y.-T. Chen, E. Ventosa, C. Scheu, A. Ludwig, W. Schuhmann (2018) Discovery of a Multinary Noble Metal Free Oxygen Reduction Catalyst, Advanced Energy Materials1 802269

Patent application 10 2017 128 058.8

What Makes High-Entropy Alloys Exceptional Electrocatalysts?

GDCh Minireviews Angewandte International Edition Chemie

Electrocatalysis

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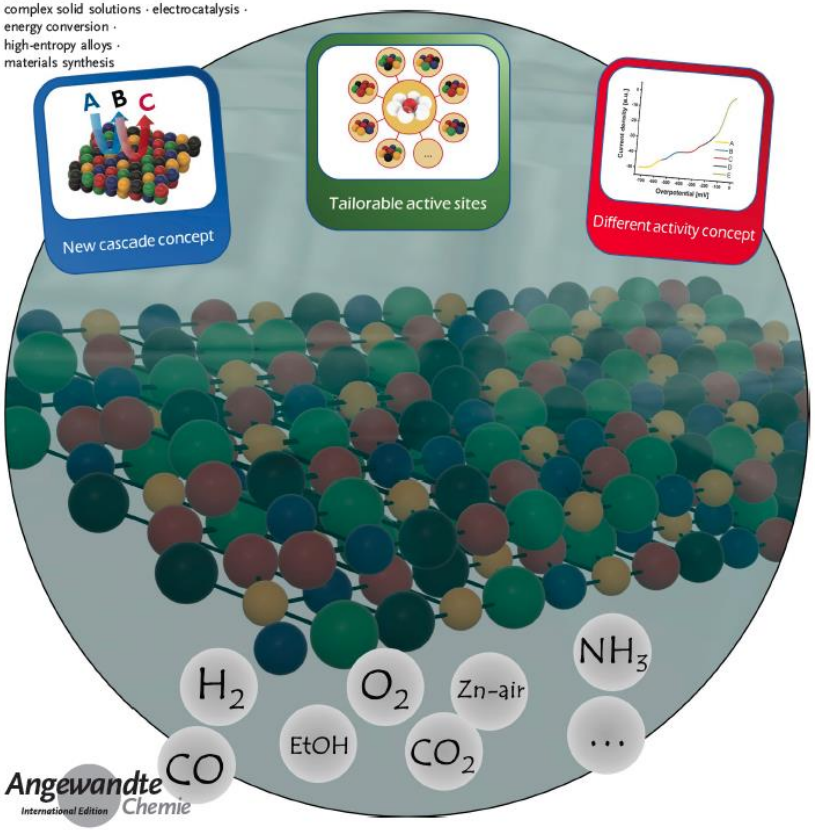
What Makes High-Entropy Alloys Exceptional Electrocatalysts?

Tobias Löffler, Alfred Ludwig, Jan Rossmeisl, and Wolfgang Schuhmann*

Keywords:
complex solid solutions · electrocatalysis · energy conversion · high-entropy alloys · materials synthesis



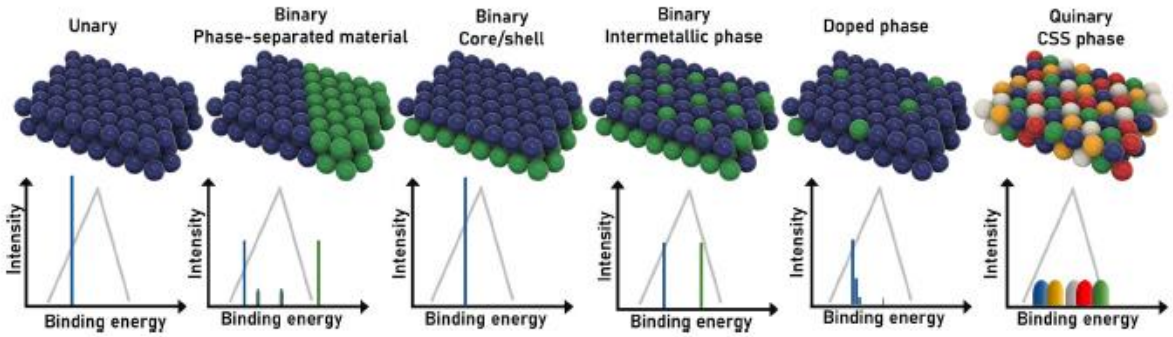


Figure 1. Schematic comparison of various kinds of catalyst surfaces with the corresponding pattern of binding energies for on-top binding of a reactant on an idealised infinite single-crystal lattice, without any step sites, edge sites, defects etc. The sum of the intensity for all peaks is the same for each scenario, yet adjusted here for better legibility.

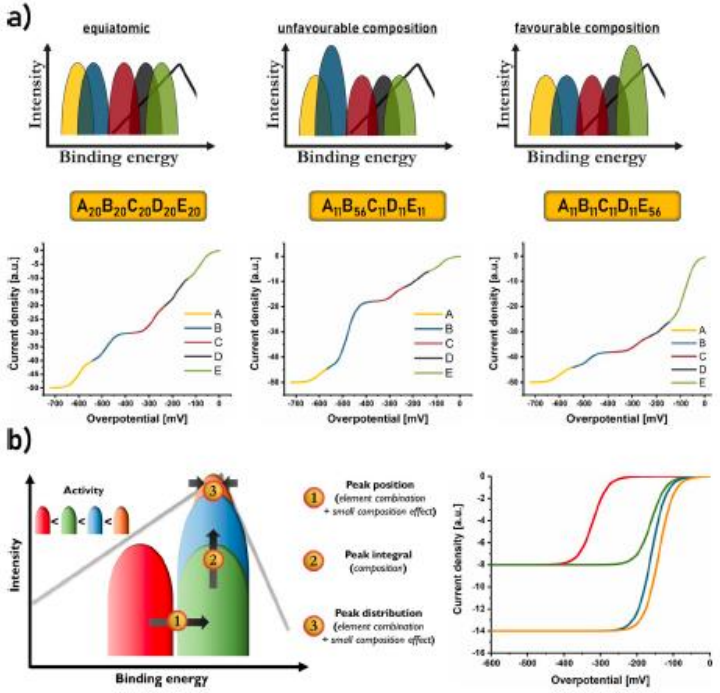


Figure 2. a) Schematic illustration of how each CCSS binding peak of the BEDP yields one current wave in voltammetric measurements, where activity and plateau current depend on binding energy shift and peak integral, respectively. Hence, adjusting the composition affects the current wave proportions. In this representation, the absence of any mass-transport effects allows visibility of all current waves. b) Since the most active current wave is of the highest interest, effects of element combination and composition on the binding peak are presented, and the effect on the corresponding current wave is shown.

Discovery of compositionally complex solid solutions („high entropy alloys“) for electrocatalysis

Experiment


FULL PAPER
Oxygen Reduction
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Discovery of a Multinary Noble Metal–Free Oxygen Reduction Catalyst

Tobias Löffler, Hajo Meyer, Alan Savan, Patrick Wilde, Alba Garzón Manjón, Yen-Ting Chen, Edgar Ventosa, Christina Scheu, Alfred Ludwig, and Wolfgang Schuhmann**

In the endeavor of discovering new noble metal-free electrocatalysts for the oxygen reduction reaction, noble metal–free multinary transition metal nanoparticle libraries are investigated. The complexity of such multiple principal element alloys provides access to a large variety of different elemental compositions, each with potentially unique properties. The strategy for efficient identification of novel electrocatalytically active systems comprises combinatorial co-sputtering into an ionic liquid followed by potential-assisted immobilization of the formed nanoparticles at a microelectrode which allows the evaluation of their intrinsic electrocatalytic activity in alkaline media. A surprisingly high intrinsic activity is found for the system Cr–Mn–Fe–Co–Ni, which is at least comparable to Pt under the same conditions, an unexpected result based on the typical properties of its constituents. Systematic removal of each element from the quinary alloy system yields a significant drop in activity for all quaternary alloys, indicating the importance of the synergistic combination of all five elements, likely due to formation of a single solid solution phase with altered properties which enables the limitations of the single elements to be overcome. Multinary transition metal alloys as a novel material class in electrocatalysis with basically unlimited possibilities for catalyst design, targeting the replacement of noble metal–based materials, are suggested.

1. Introduction

The oxygen reduction reaction (ORR), as a key reaction in electrocatalysis, attracts considerable attention due to its complex

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DOI: 10.1002/aenm.201802269

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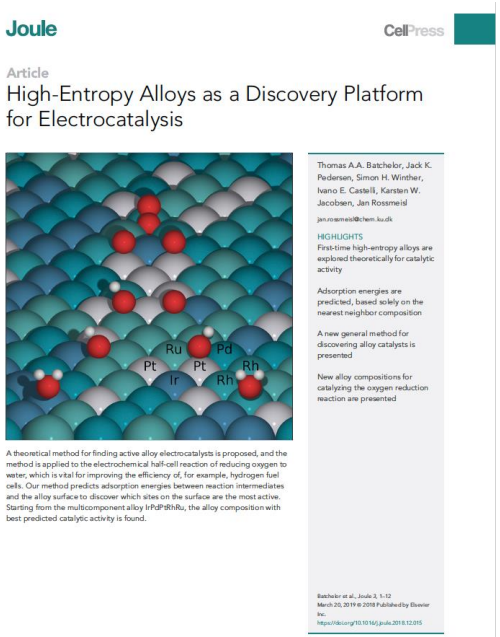
four-electron/four-proton transfer, which causes sluggish kinetics. Pt-based materials are the state-of-the-art electrocatalysts for ORR due to their outstanding catalytic activity, selectivity, and long-term stability under operating conditions.[1] However, their scarcity and, thus, high cost limit their applications.

Accordingly, research on non-noble metal catalysts increased substantially over the past decades. The most promising material classes so far are transition-metal–nitrogen–carbon complexes[2–4] with Fe or Co as the metal center,[5,6] metal–N_4 organometallic complexes[7] or metal-free catalysts such as nitrogen-doped carbon species utilizing carbon nanotubes or graphene.[8–10] These catalysts show promising activity; however, they still fall short in their overall performance compared to Pt. Hence, new materials capable of replacing Pt-based catalysts for ORR are yet to be found.

One approach in exploring novel materials is to increase their chemical complexity. Multinary metal alloys require a more challenging synthesis pathway, but enable a virtually unlimited amount of different compositions. For instance, over 2×10^8 combinations for quinary alloys selected from a list of 50 elements are possible, each with a different composition. Therefore, selection of candidate materials to be tested is necessary, e.g., based on abundance and toxicity of elements. Some of these largely unexplored multinary compositions might show unique physical and chemical properties. For many alloys, comprising typically five principal elements or more, an unexpected stability as a single solid solution phase was observed in spite of their chemical complexity. This stability is usually explained by the so-called high-entropy effect.[11–13] The proposed underlying rational include i) stabilization of the multinary single phase due to increasing entropy with an increasing number of constituents, ii) a lattice distortion effect, and iii) sluggish diffusion.[14] This special state of a complex solid solution may result in unusual properties which are not observed for heterogeneous multiphase alloys comprising intermetallic phases. Their advantages in mechanical, physical, and chemical properties such as structural stability[15] as well as corrosion[16] and oxidation resistance have been evaluated over the past years.[17] Potential applications in (electro)catalysis have only been reported for

Adv. Energy Mater. 8, 1802269 (2018)

Simulation


Joule
CellPress

Article

High-Entropy Alloys as a Discovery Platform for Electrocatalysis

Thomas A.A. Batchelor, Jack K. Pedersen, Simon H. Winther, Ivano E. Castelli, Karsten W. Jacobsen, Jan Rossmeisl

jan.rossmeisl@chem.ku.dk

HIGHLIGHTS

First-time high-entropy alloys are explored theoretically for catalytic activity

Adsorption energies are predicted, based solely on the nearest neighbor composition

A new general method for discovering alloy catalysts is presented

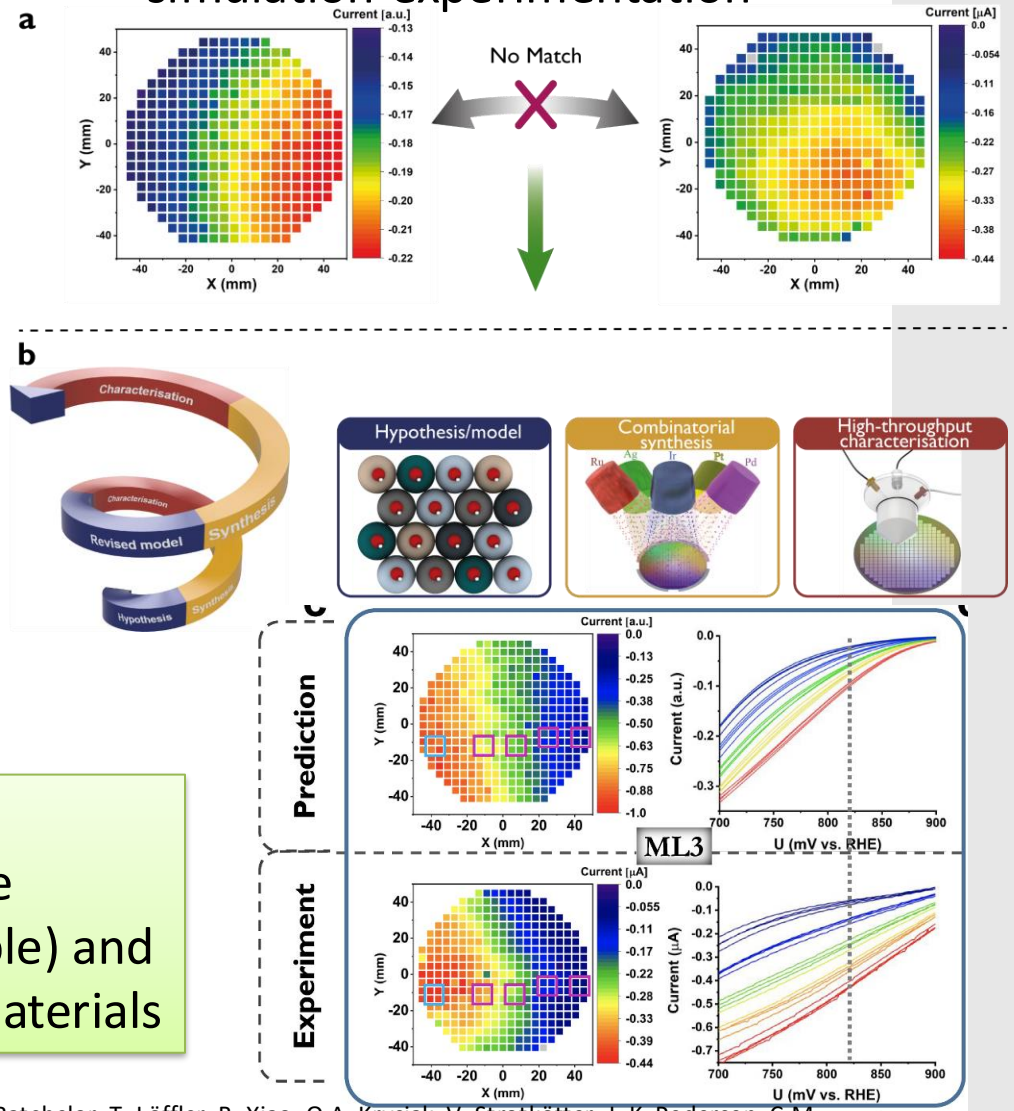
New alloy compositions for catalyzing the oxygen reduction reaction are presented

A theoretical method for finding active alloy electrocatalysts is proposed, and the method is applied to the electrochemical half-cell reaction of reducing oxygen to water, which is vital for improving the efficiency of, for example, hydrogen fuel cells. Our method predicts adsorption energies between reaction intermediates and the alloy surface to discover which sites on the surface are the most active. Starting from the multicomponent alloy IrPdPtRhRu, the alloy composition with best predicted catalytic activity is found.

Batchelor et al., Joule 2, 1–12
March 20, 2019 © 2018 Published by Elsevier Inc.
https://doi.org/10.1016/j.joule.2018.12.015

Joule (2018)

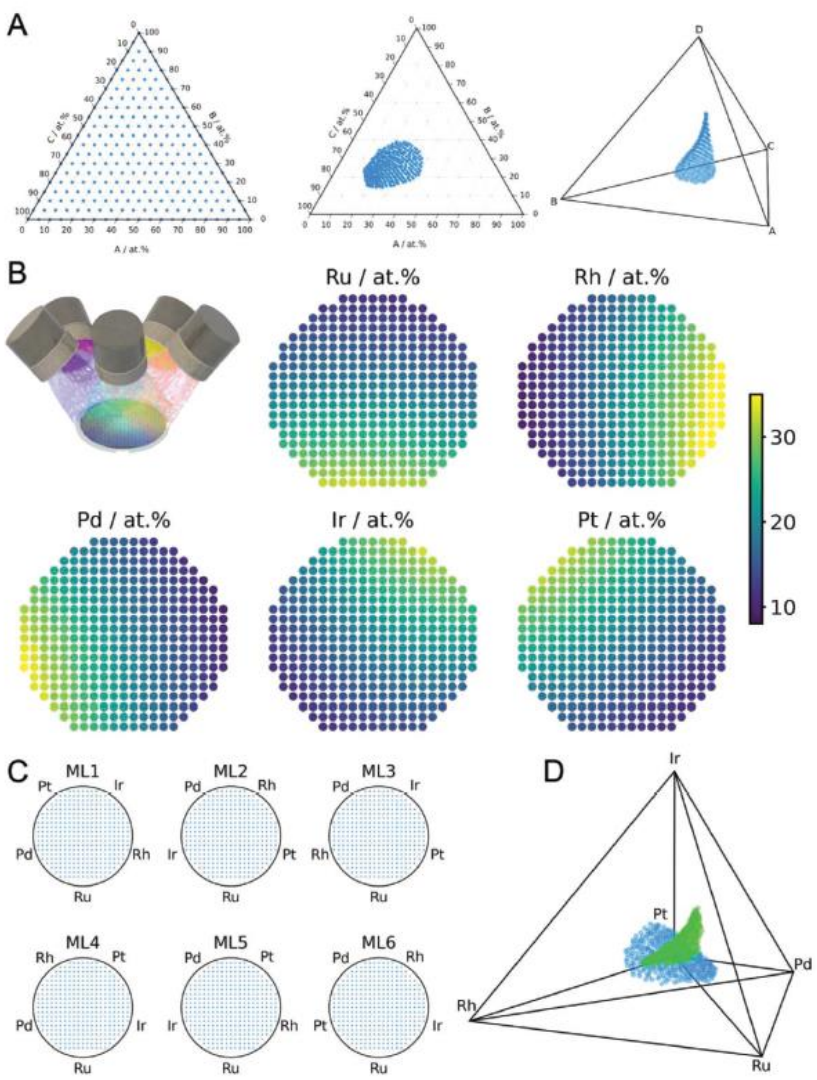
Closed-loop simulation-experimentation

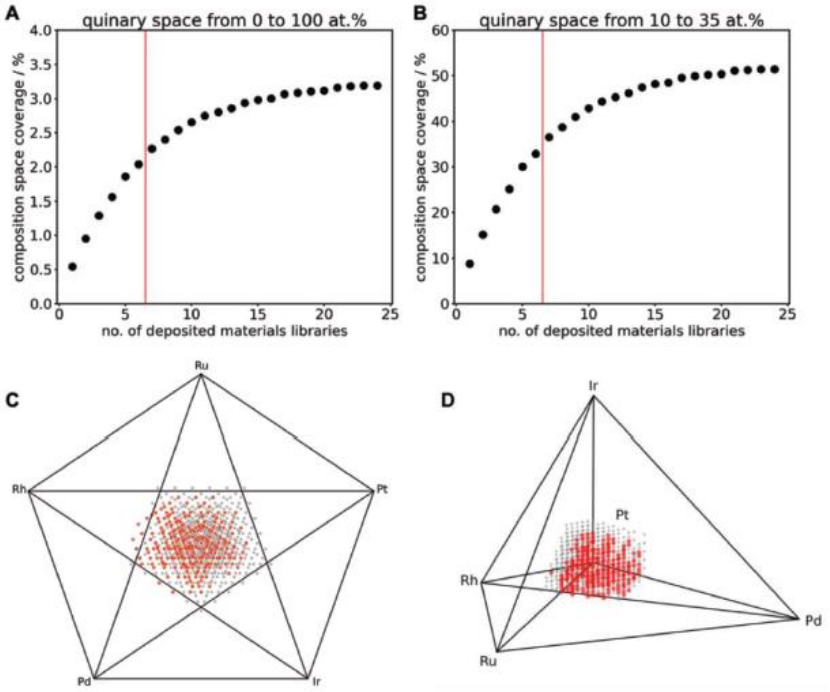


We need fast methods to explore
the multidimensional CSS search space
to identify new electrocatalysts (active + stable) and
understand the working principles of these materials

T. A. A. Batchelor, T. Löffler, B. Xiao, O.A. Krysiak, V. Strotkötter, J. K. Pedersen, C.M. Clausen, A. Savan, Y. Li, W. Schuhmann, J. Rossmeisl, A. Ludwig *Complex solid solution electrocatalyst discovery by prediction and high-throughput experimentation*, Angewandte Chemie Int Ed (2021) 60, 6932–6937

Unravelling composition-activity-stability trends in high entropy alloy electrocatalysts using a data-guided combinatorial synthesis strategy and computational modelling





L. Banko, O. A. Krysiak, J. K. Pedersen, B. Xiao, A. Savan, T. Löffler, S. Baha, J. Rossmeisl, W. Schuhmann, A. Ludwig (2022) *Unravelling composition-activity-stability trends in high entropy alloy electrocatalysts by using a data-guided combinatorial synthesis strategy and computational modelling*, Advanced Energy Materials, 2103312

Questions

(1) What are “high entropy alloys“?

(2) Why is the name in some cases problematic?

(3) What is the promise of high entropy materials?

(4) What makes high entropy nanomaterials interesting?

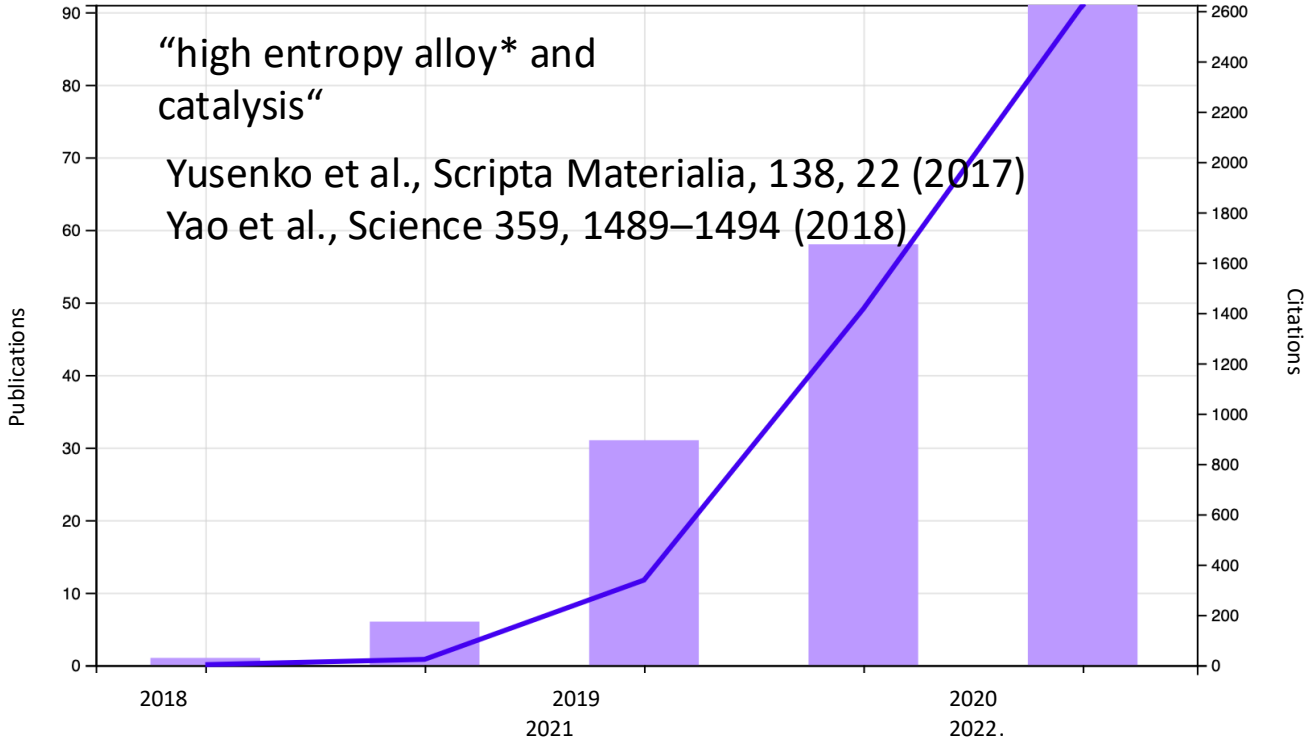
(5) Discuss (meta)stability and phase formation in the context of HEAs

Neue Großprojekte zur Erforschung von Hochentropie-Materialien für das Energiesystem der Zukunft

Alfred Ludwig

Ruhr-Universität Bochum

Discovery: Cr-Mn-Fe-Co-Ni rivals Pt in oxygen reduction reaction



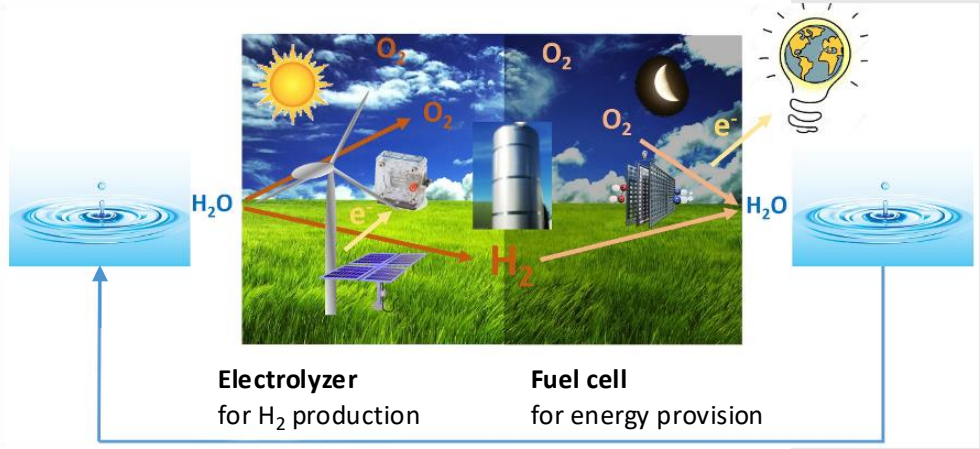
T. Löffler, H. Meyer, A. Savan, P. Wilde, A. Garzón Manjón, Y.-T. Chen, E. Ventosa, **C. Scheu, A. Ludwig, W. Schuhmann** (2018)
Discovery of a Multinary Noble Metal Free Oxygen Reduction Catalyst,
Advanced Energy Materials 1 802269

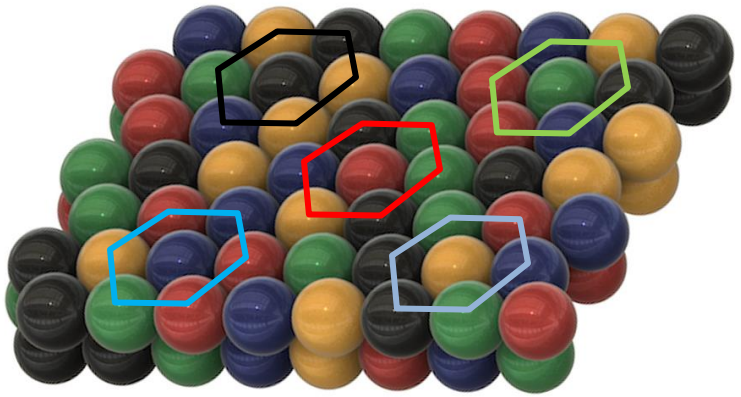
T. Batchelor, J. Pedersen, S. Winther, I. Castelli, K. Jacobsen, **J. Rossmeisl** (2019)
High-Entropy Alloys as a Discovery Platform for Electrocatalysis,
Joule, 2019, 3, 834

Motivation for compositionally complex solid solutions (CCSS) and surface atom arrangements (SAA)

Goal of
Collaborative Research Centre 1625
fundamental scientific understanding
of CCSS surfaces,
i.e. mastering poly-elemental SAA
by fusion of simulation,
synthesis,
characterisation,
and data science

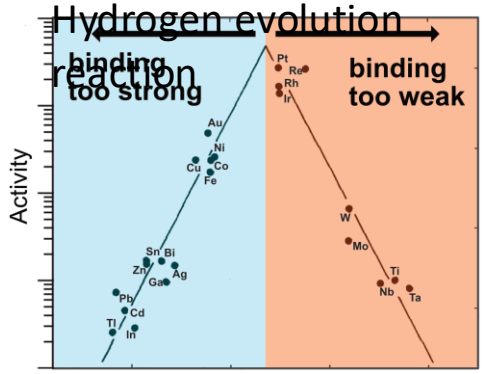
1.4.2024- 31.12.2027 (+ 2 x 4 years)





SAA make CCSS exceptional electrocatalysts

Example:
Hydrogen evolution reaction



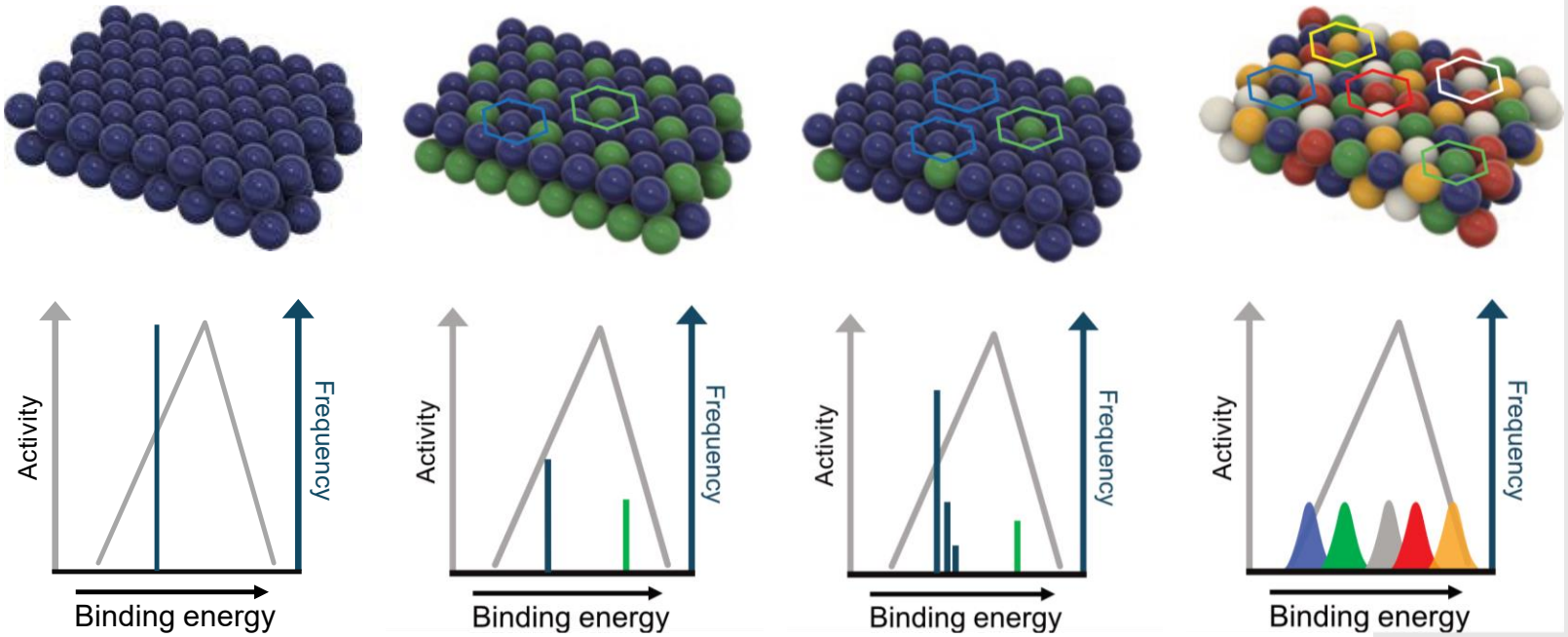
Binding energy as descriptor for catalytic activity

Single element
(ideal surface)

Binary intermetallic phase

Doped phase

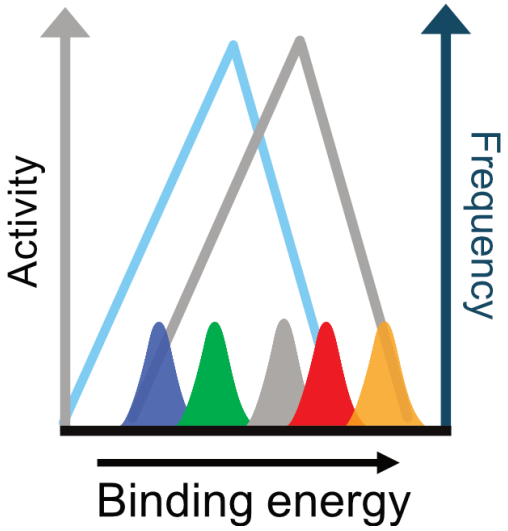
Quinary CCSS phase

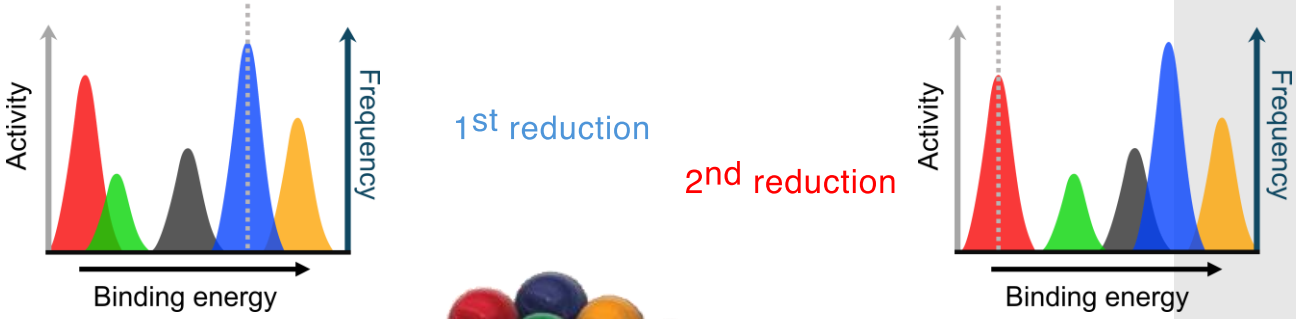


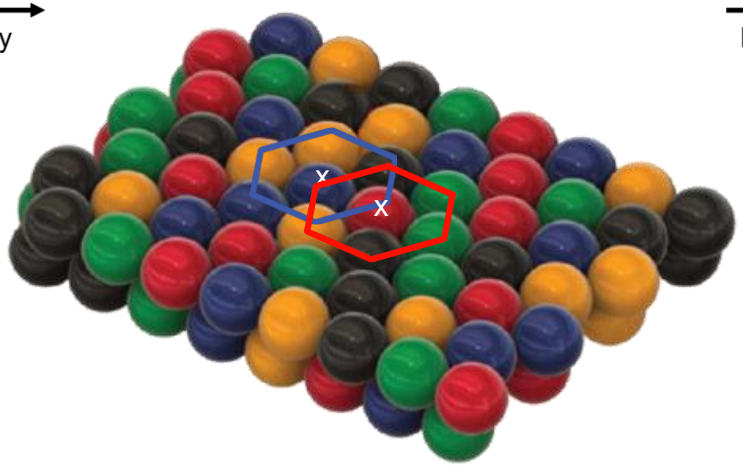
T. Löffler, **A. Ludwig, J. Rossmeisl, W. Schuhmann** (2021) *What makes high-entropy alloys exceptional electrocatalysts?* Angew. Chem. Int. Ed. 2021, 60, 26894

Universal applicability and multifunctionality of CCSS

Hypothesis
Electrochemical properties of CCSS can be tailored for any reaction,
if we can master their poly-elemental surface atom arrangements







Multifunctional CCSS surface

Activity and stability **Cascade reactions**

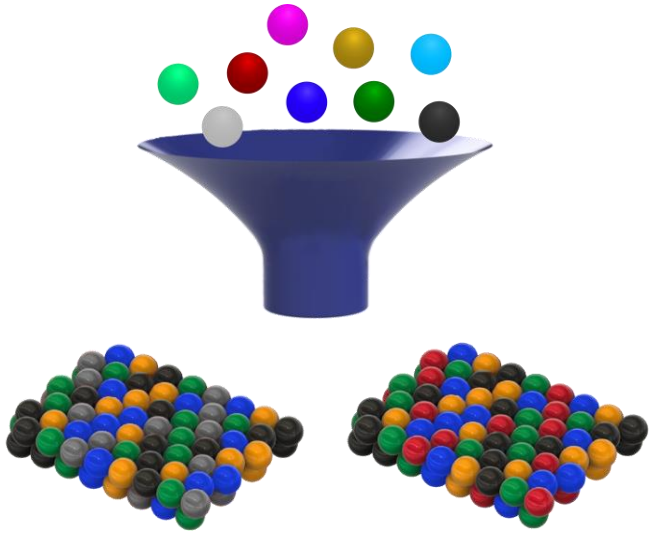
Exploration and exploitation of CCSS by data-driven science

→ **Identify most active SAA**
→ **Maximise their number**

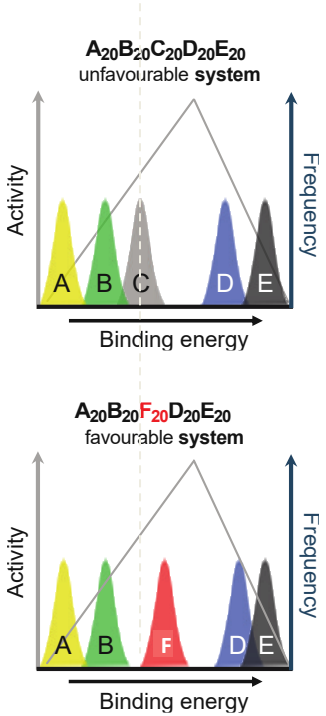
Phase I:

- 9 noble metals
- 126 quinary systems
- 10^4 compositions in 1 system
- 10^5 of SAA for 1 composition

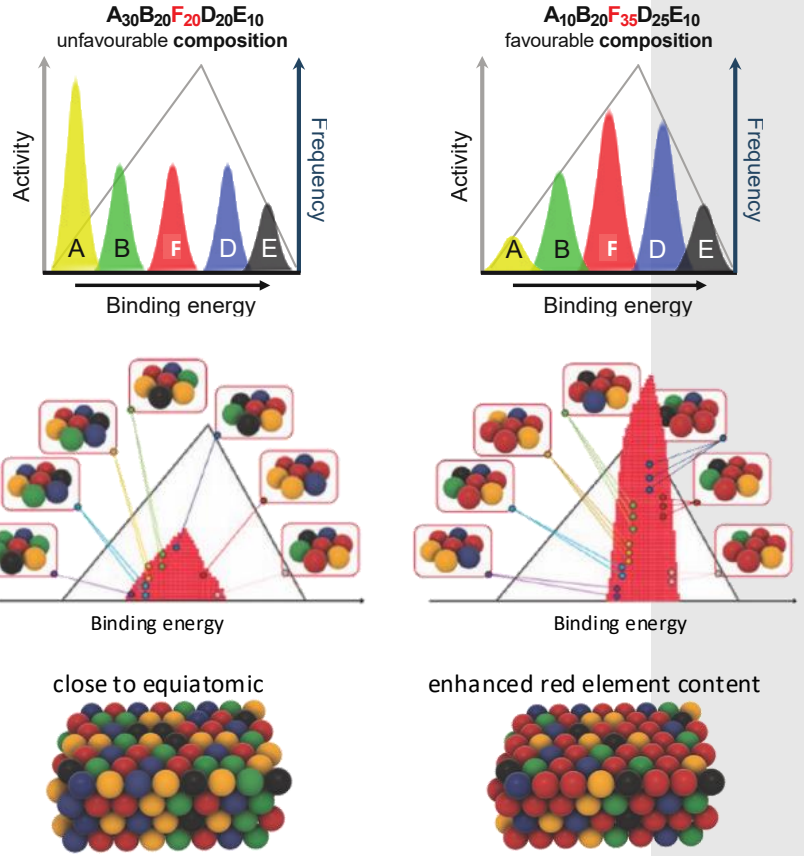
Combinatorial explosion
→ data-driven science



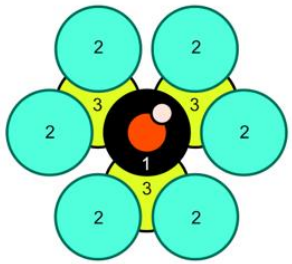
System selection

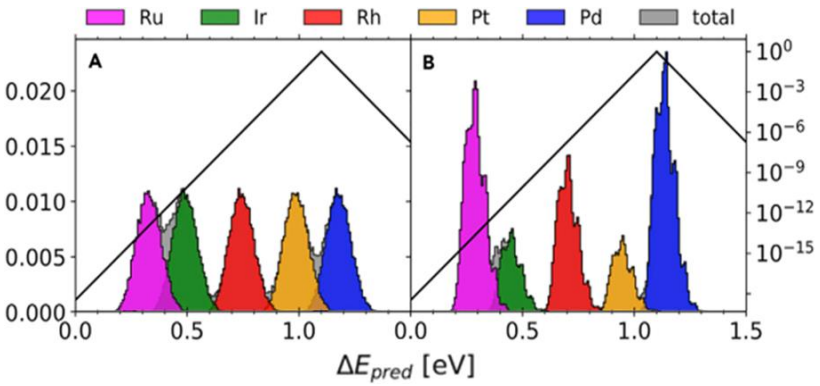


Composition optimisation



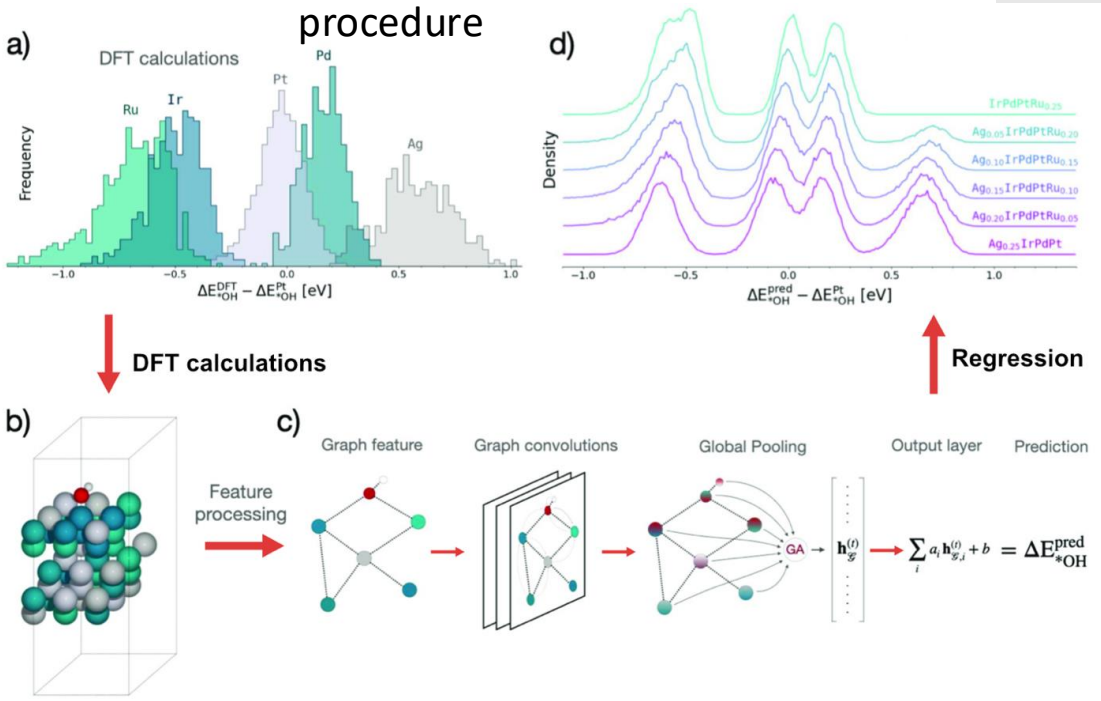
Theoretical basis for understanding and rational design of SAA





T. Batchelor, J. Pedersen, S. Winther, I. Castelli, K. Jacobsen, **J. Rossmeisl**, Joule, 2019, 3, 1

Adsorption energy regression procedure



C.M. Clausen, M.L.S. Nielsen, J.K. Pedersen, **J. Rossmeisl** (2022) *Ab Initio to Activity: Machine Learning-Assisted Optimization of High-Entropy Alloy Catalytic Activity*, High Entropy Alloys & Materials

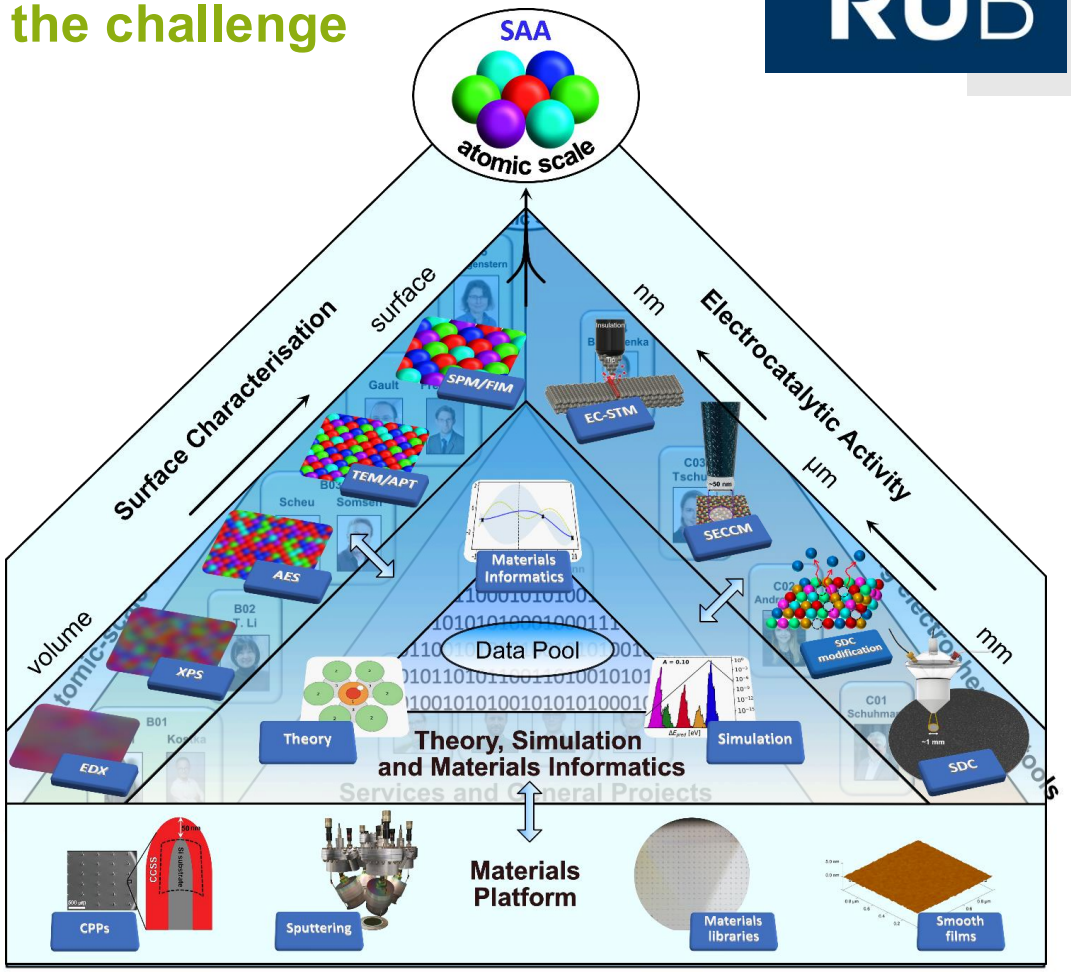
CRC 1625: A unique team to address the challenge

Scale-bridging approach integrating

- **theoretical prediction**
- **high-throughput and in-depth experiments**
- **data science**

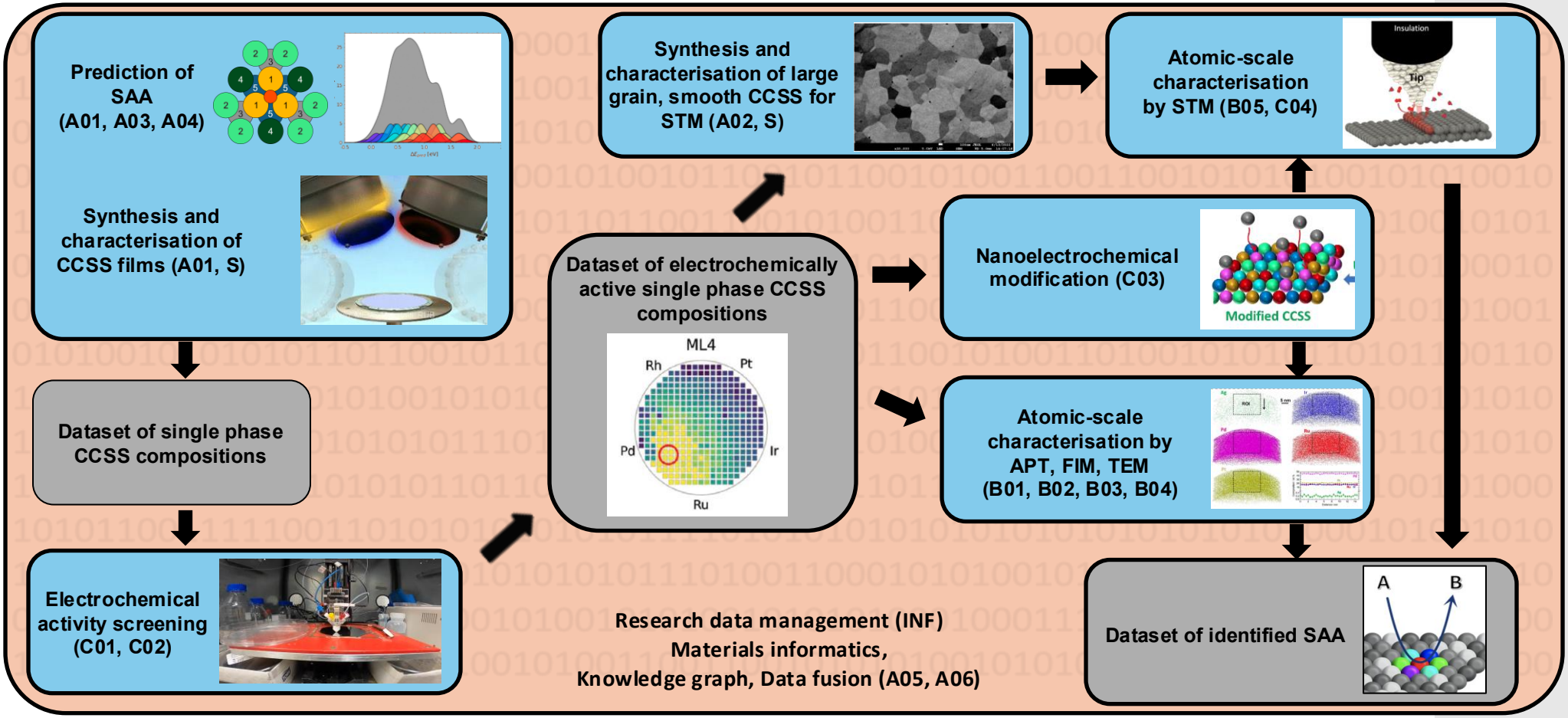
Atomic-scale details
and
statistical abundance
of SAA

Deep collaboration
Sample and data lineage tracking



A: Theory, simulation, data-guided design and synthesis of CCSS surfaces

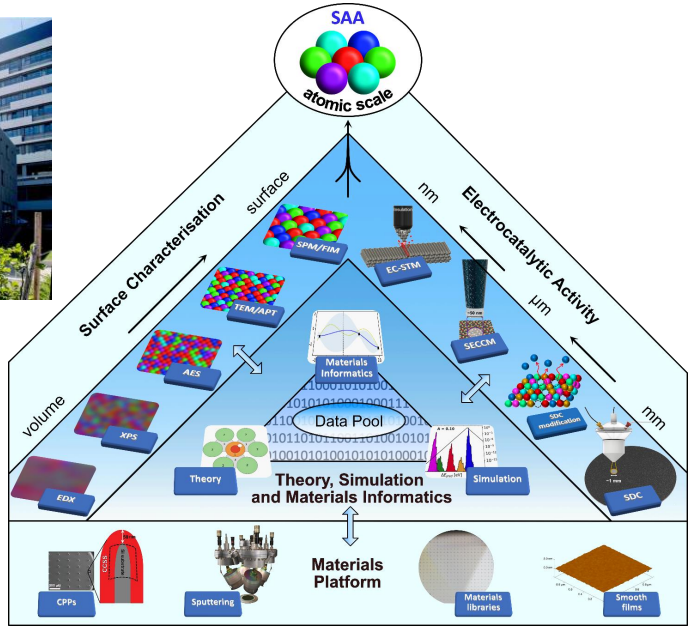
Exemplary workflow to identify SAA: Data-guided prediction-synthesis-characterisation

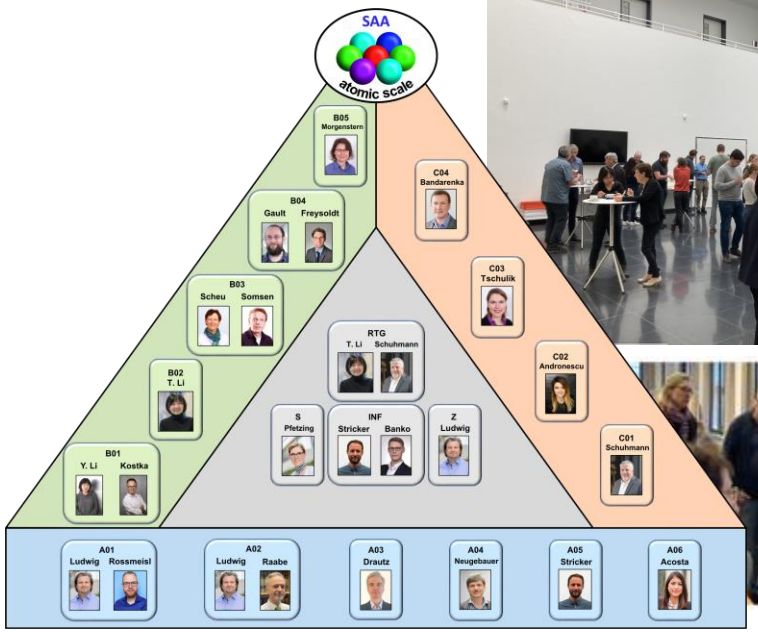


CRC 1625

Atomic-scale understanding and design of multifunctional compositionally complex solid solution surfaces

RUB





Our holistic approach will fulfil the vision to control SAA on the atomic scale and across the surface and enable design of ideal CCSS surfaces for specific applications

ERC Synergy Grant DEMI

UNIVERSITY OF COPENHAGEN

UNIVERSITÄT BERN

RUHR UNIVERSITÄT BOCHUM

RUB

HI ERN Helmholtz Institute Erlangen-Nürnberg part of Forschungszentrum Jülich

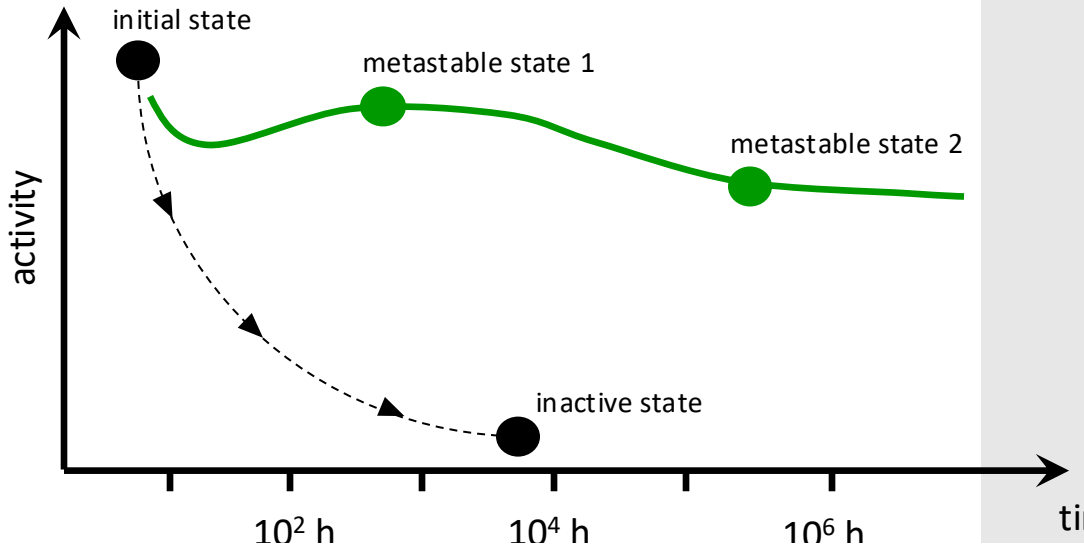
2024 - 2029

- High activity
- Natural abundance
- Stable

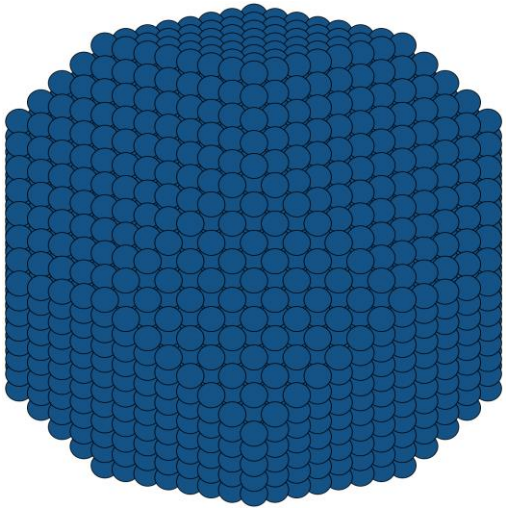
21	22	23	24	25	26	27	28	29	30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
39	40	41	42	43	44	45	46	47	48
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
71	72	73	74	75	76	77	78	79	80
Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
103	104	105	106	107	108	109	110	111	112
Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn

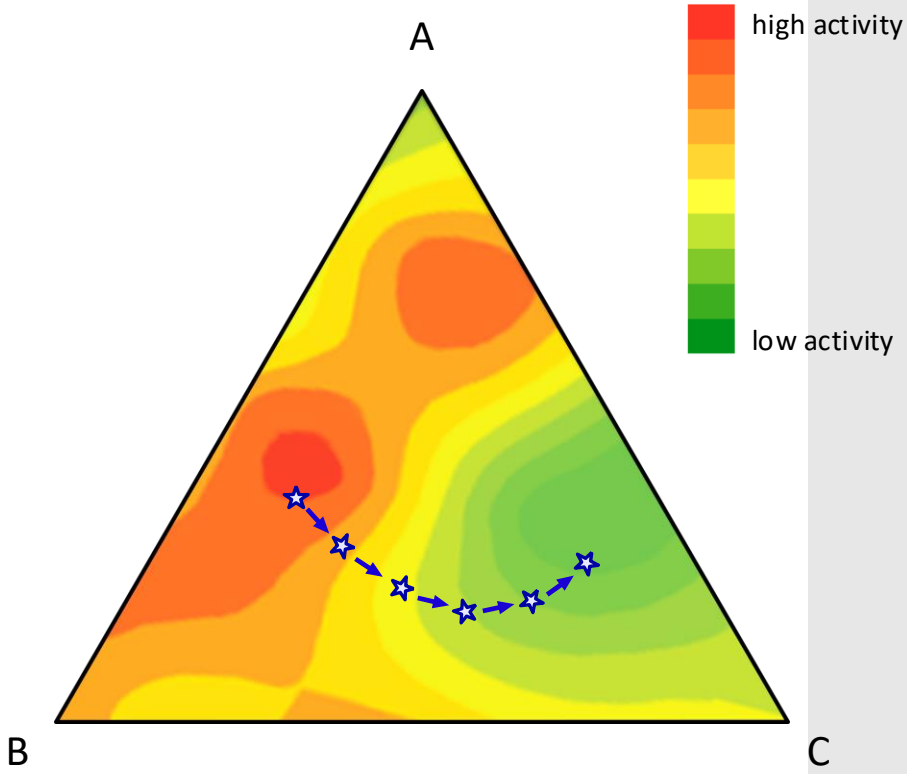
Oxygen reduction reaction
Oxygen evolution reaction
CO_2 reduction reaction

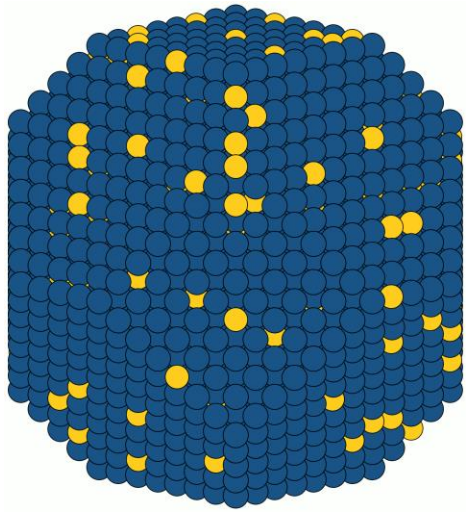
- Uncontrolled degradation
- Complex materials space
- No theory of metastability

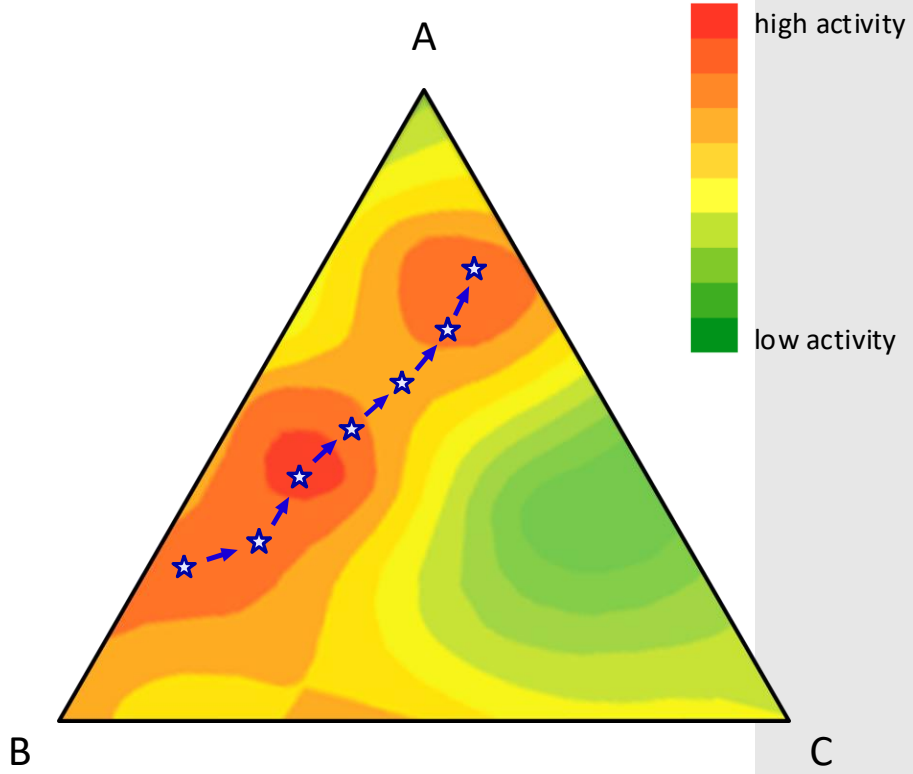


High entropy material nanoparticle
(all elements shown in blue)



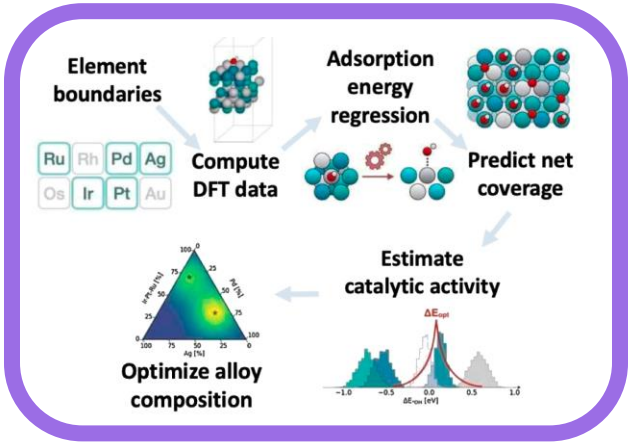


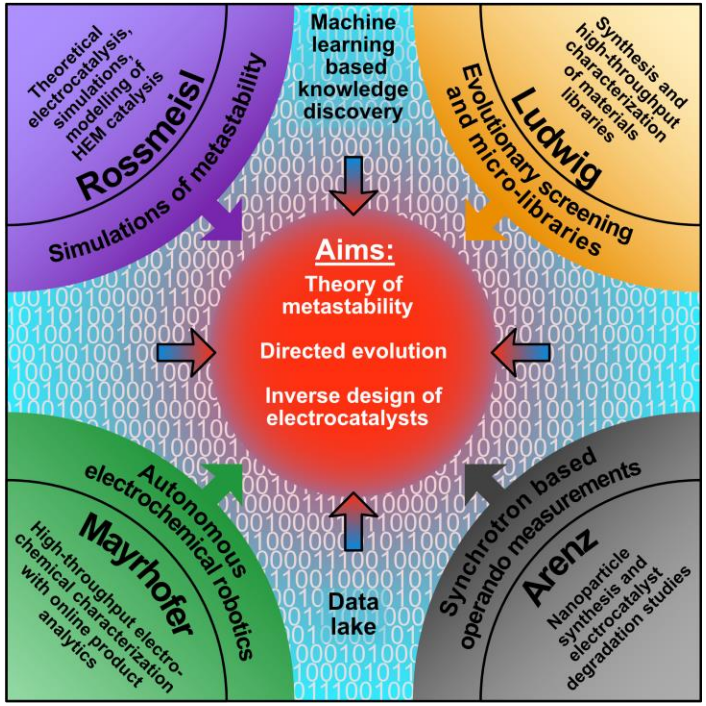


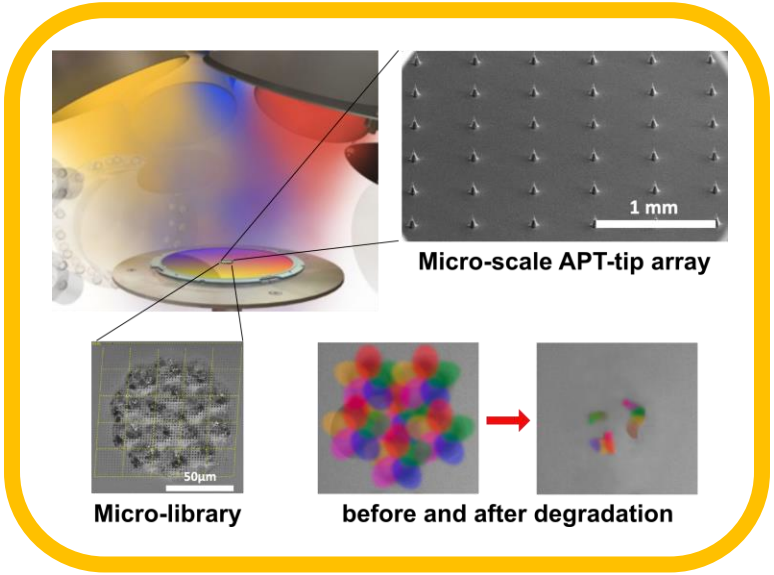


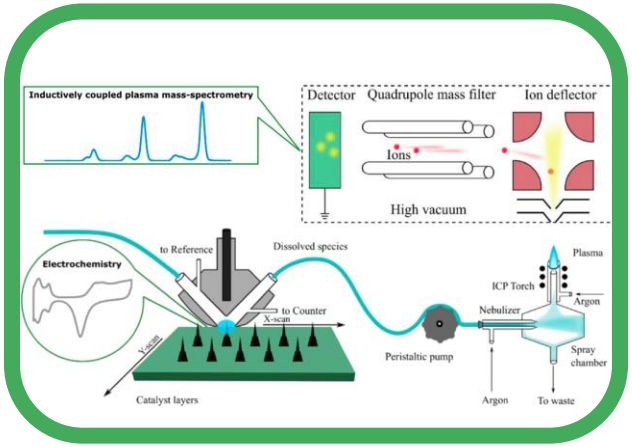
Ludwig, Mayrhofer et al. Nature Catalysis 2018; **Arenz, Rossmeisl** et al. in review

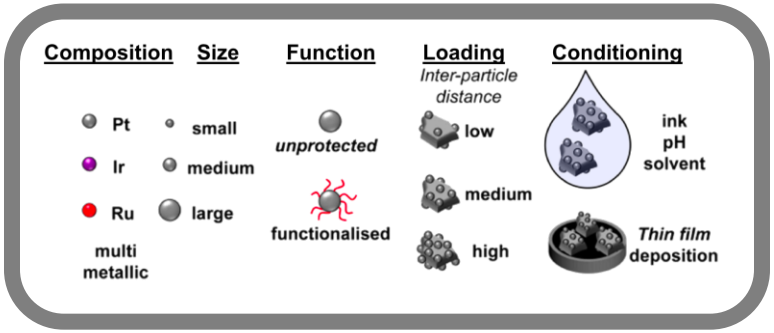
KAPITEL | CHART-HEADLINE











New approaches for Accelerated Materials Discovery

- **Microlibraries**

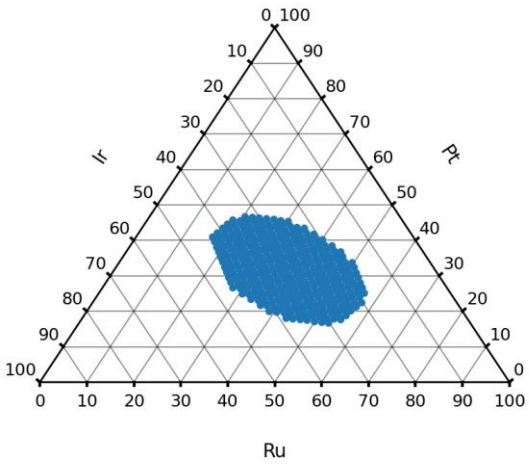
- **Combinatorial processing platforms for accelerated atomic scale characterization**

Part of ERC Synergy Project DEMI
Directed Evolution of Metastable Electrocatalyst Interfaces for Energy Conversion
(J. Rossmeisl, Copenhagen; M. Arenz, Bern; A. Ludwig, Bochum; K. Mayrhofer, Erlangen)

Funded by the European Union
European Research Council
Established by the European Commission

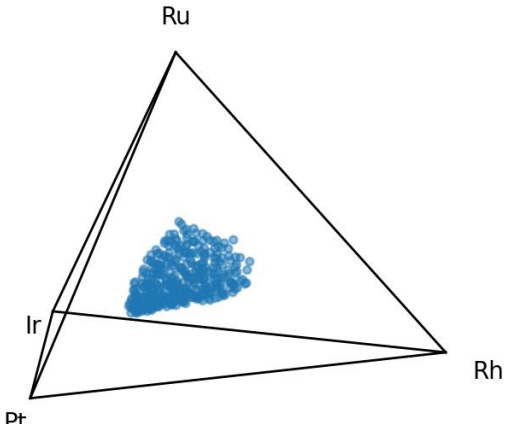
Exploring the quinary composition space

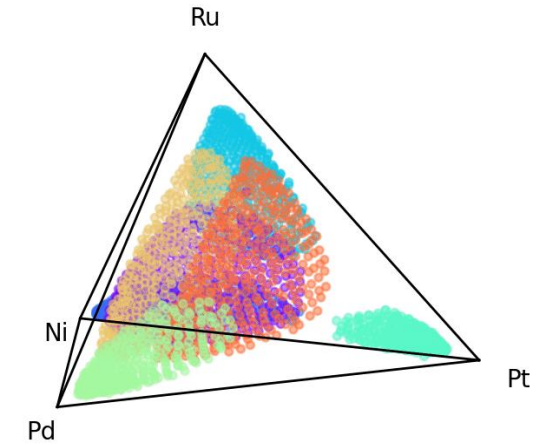
ternary: Ir-Pt-Ru



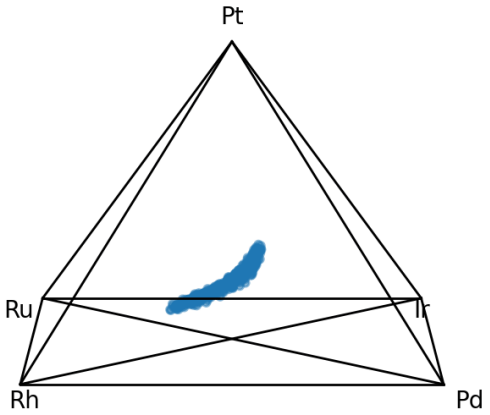
coverage: 17%

quaternary: Ir-Pt-Ru-Rh





quinary: Ir-Pt-Ru-Rh-Pd



coverage: 0.6%

L. Banko, E. B. Tetteh, A. Kostka, T. H. Piotrowiak, O. A. Krysiak, U. Hagemann, C. Andronescu, W. Schuhmann, A. Ludwig (2023)
Microscale combinatorial libraries for the discovery of high entropy materials, Advanced Materials, 2207635

New approach: Micro-Libraries

RUB

Co-sputtering through a single | Creating a micro-library by

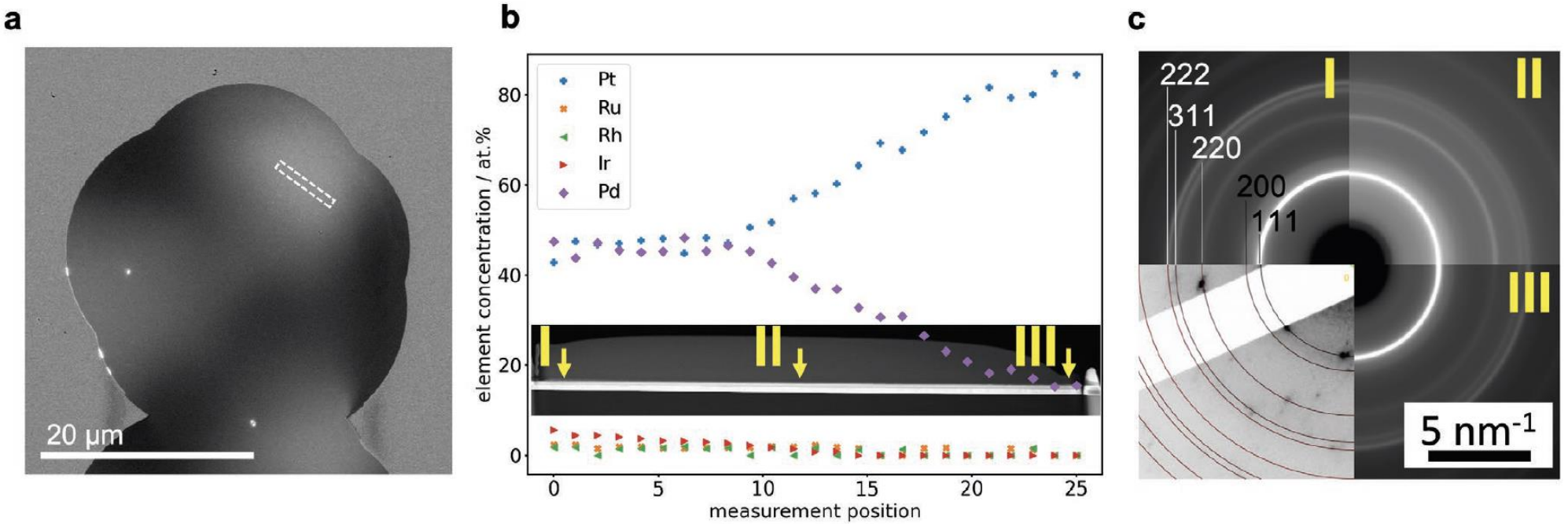
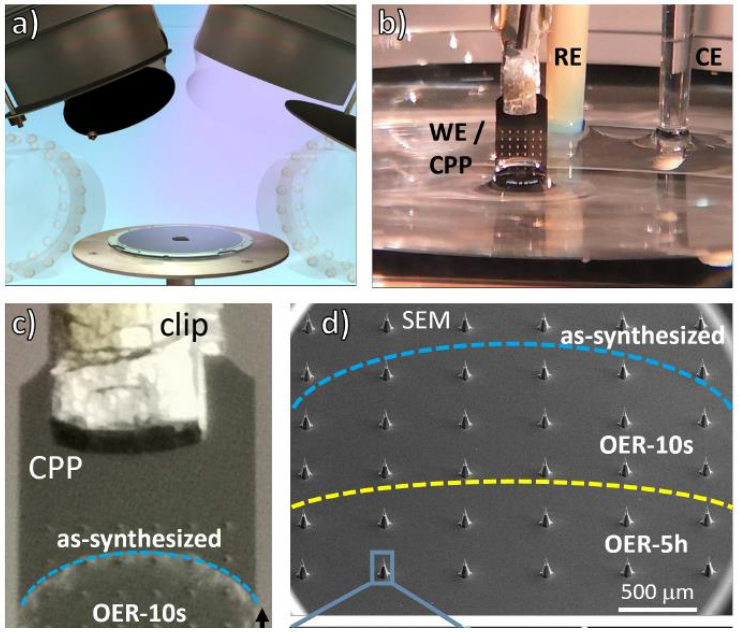


Figure 2. High-throughput nanoscale characterization of microlibraries. a) SEM image of a microlibrary. The position of the FIB-cut cross-sectional sample is indicated. b) Chemical composition along the FIB-cut sample from TEM–EDX. The positions where the diffraction patterns were acquired are highlighted on the high angle annular dark field TEM cross-sectional image (inset). c) Averaged diffraction patterns from the regions highlighted in panel (b) as well as an exemplary raw diffraction pattern with overlaid Pt lines.

L. Banko, E. B. Tetteh, A. Kostka, T. H. Piotrowiak, O. A. Krysiak, U. Hagemann, C. Andronescu, W. Schuhmann, A. Ludwig (2023) *Microscale combinatorial libraries for the discovery of high entropy materials*, Advanced Materials, 2207635

Combinatorial processing platforms for accelerated phase evolution in HEM: Electrochemical Oxidation



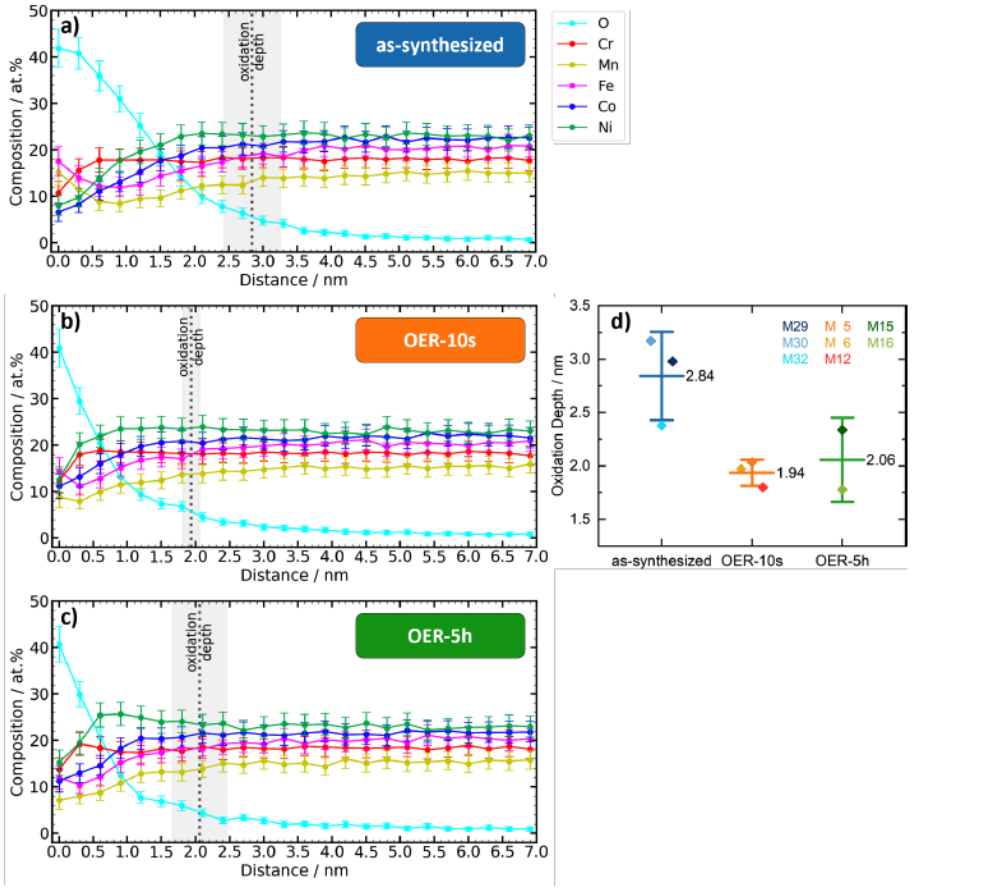


Fig. 3 | Oxidation depths. a-c, Element composition vs depth plots of the different states. Dashed lines indicate the mean oxidation depth with a standard deviation beyond which the oxygen content remains at low values. **d**, Plot of the oxidation depths of the different states with mean value and standard deviation. Each tip is represented by a different color.

V. Strotkötter, Y. Li, F. Lourens, A. Kostka, T. Löffler, W. Schuhmann, A. Ludwig (2024) *Self-Formation of Compositionally Complex Surface Oxides on High Entropy Alloys Observed by Accelerated Atom Probe Tomography: A Route to Sustainable Catalysts*, Materials Horizons, 11, 4932-4941, 10.1039/D4MH00245H

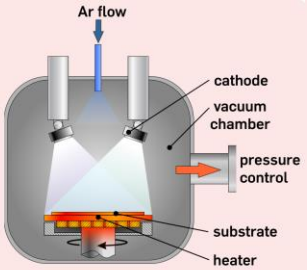
Summary and Outlook

Materials discovery and optimization

Consistent and complete multidimensional data-sets of compositionally complex materials

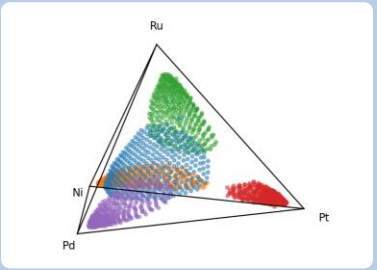
RUB

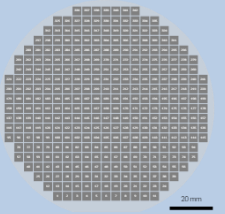
Synthesis of thin film materials libraries



High-throughput characterization

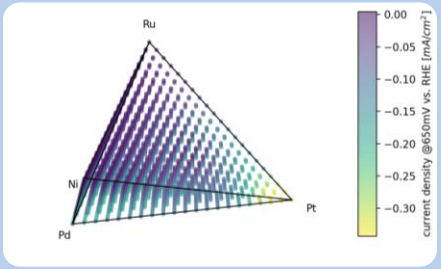
- EDX
- XRD
- 4PP
- SDC
- ...

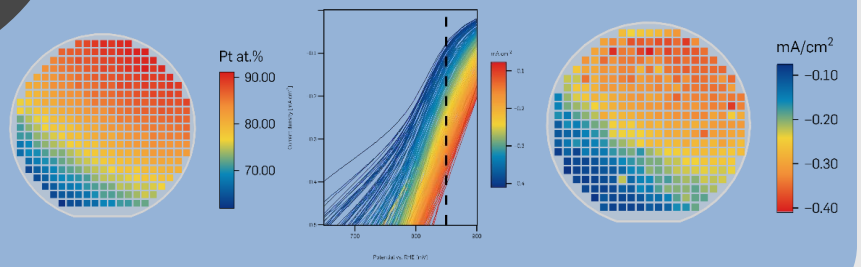




Combinatorial Materials Science Loop

Planning of next experiment





Start-up: **xemX**

Materials data management + materials informatics (AI agents) -> autonomous experimentation

Data analysis

Acknowledgments

All group members
All cooperation partners
Funding from DFG, BMBF, ERC

Funded by DFG Deutsche Forschungsgemeinschaft German Research Foundation

Funded by the European Union

erc European Research Council Established by the European Commission