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REGENERATIVE PEROVSKITES FOR A RESILIENT RESOURCE-EFFICIENT FUTURE

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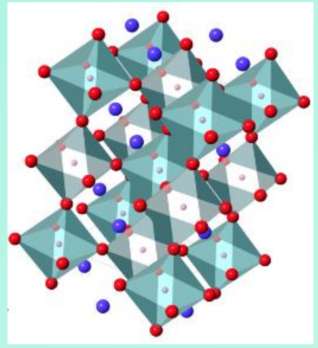
Currently, the most important and urgent challenges are directly related to energy and environmental issues. Performance degradation or aging behavior in energy conversion and storage materials has been the focus of many research areas. Research in halide perovskite solar cells has exhibited that the stability is still below the requirements for a commercial application. Rechargeable batteries become less effective as they chemically age. The best water splitting materials for the electrocatalytic oxygen evolution reaction should balance stability and activity. Solid oxide fuel cells for electricity generation and solid oxide electrolysis cells for H_2 production are not commercialized mainly due to cell durability let alone the costs. All the examples listed above imply that it is not easy to obtain materials with enhanced life time and better performance simultaneously, let alone the sustainability and security into consideration. In this regard, developing materials which can be regenerated, self-repaired, and self-healed remains a critical challenge. In this work, as one of the examples, regenerative behavior of perovskite-type oxides will be presented. Different perovskite-type oxides with regenerative properties were studied by thermogravimetric analysis and *in situ* X-ray diffraction. The correlation between oxidation-reduction reaction and crystal lattice changes is discussed. It is anticipated that this finding and understanding would serve as an initial platform to develop strategies to circumvent the paradox of efficiency and stability, opening up opportunities and approaches to produce the highly active energy converters with a desired lifetime from available resources.

I. Perovskite, $ABO_{3-\delta}$

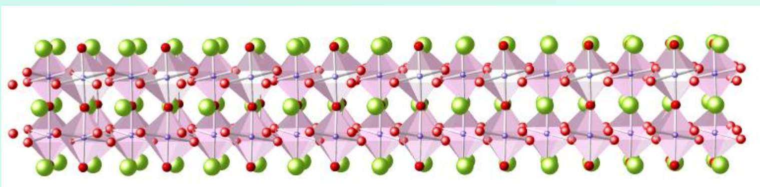


- Profound flexibility & tolerance matter: composition, atomic & crystal structure, microstructure (morphology, pore structure)
- Defects (mostly vacancies)
- Activity and stability issues in various applications

II. Research goals and questions

- Development of functional perovskite-type materials based on reversible & regenerative chemical reactions
- Reversible formation and migration of oxygen vacancies in various perovskite-type oxides
- How can we control the onset temperature of oxygen uptake/release & make it reversible ?
- A tailor-made perovskites system for targeted energy conversion and storage ?

Requested material properties
- Redox active
- Reversible
- Selective
- Dynamically defective

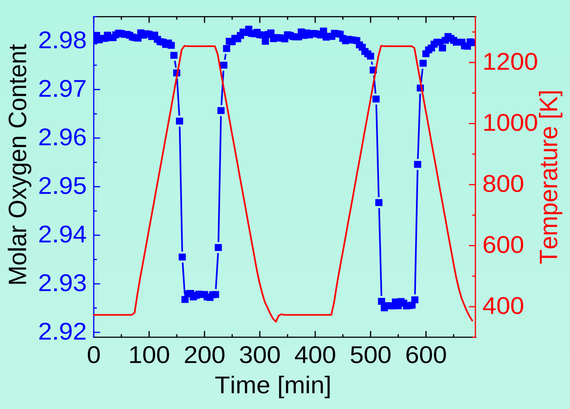


perovskites have been widely used

Applications including
- SOFC/SOEC
- Membranes
- Heterogeneous catalysts
- Thermoelectric converters
- Solar fuels

III. Reversible redox reactions

Case 1. $CaMnO_{3\pm\delta}$ @ 1273 – 1373 °C for thermoelectric converters

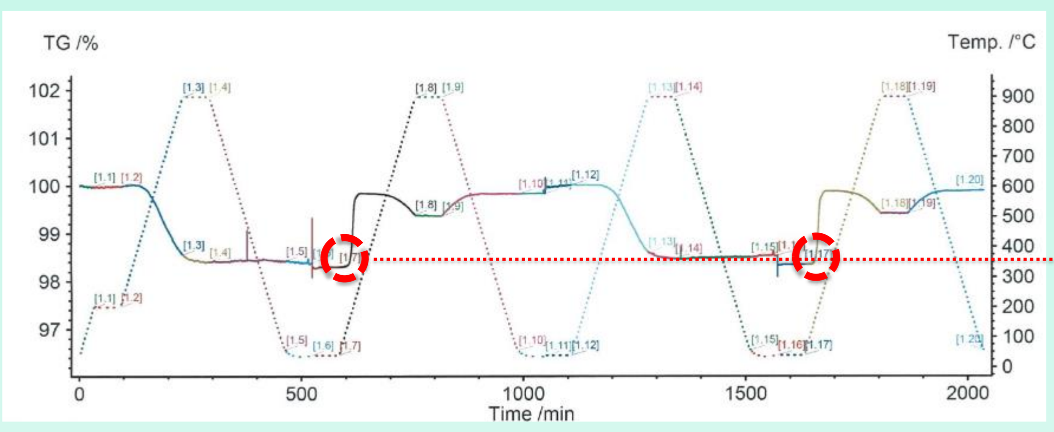


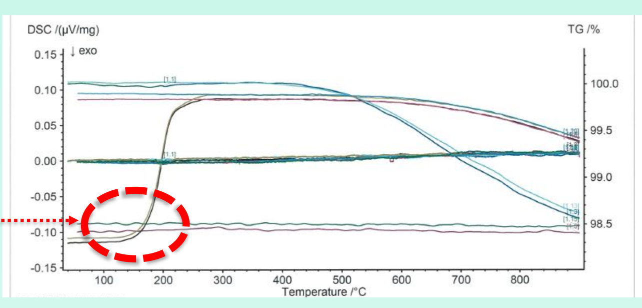
- Reduction of W-substituted $CaMnO_{3\pm\delta}$
- → oxygen loss and uptake
- → generated charge carriers with enhanced thermoelectric properties
- Regeneration / entirely reversible process
- → monitored by thermogravimetric analysis

Thiel, Weidenkaff et al. *J. Appl. Phys.* **2013**, 114, 243707

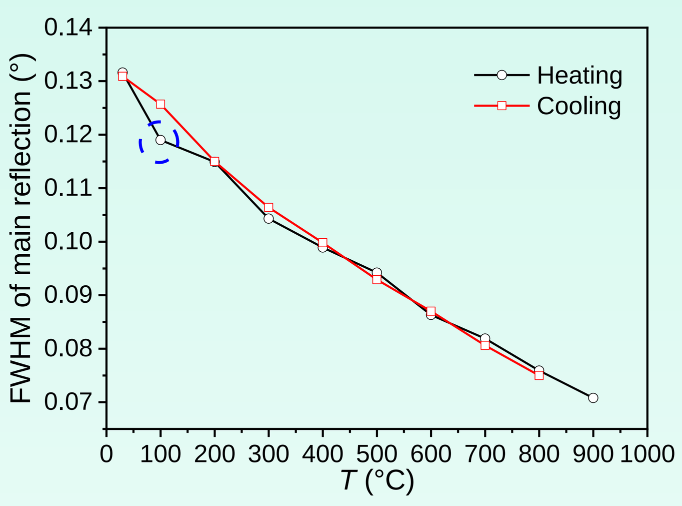
Case 2. $(La,Sr)FeO_{3-\delta}$ nanoparticles @ 150 °C

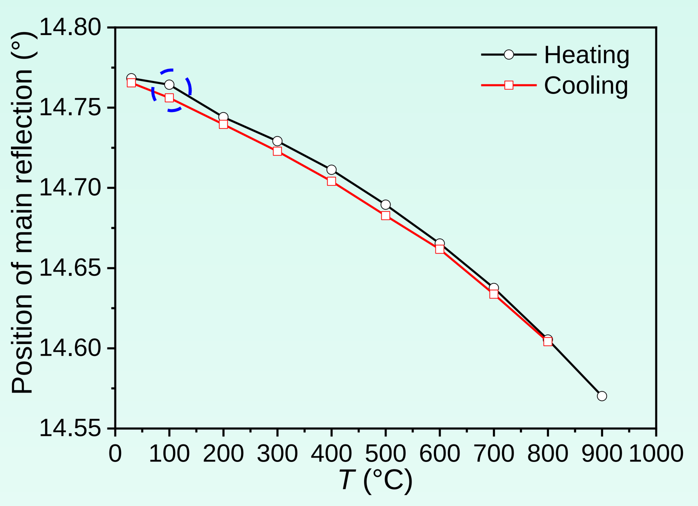
- Thermogravimetric analysis: entirely reversible, regenerative oxygen loss and uptake was monitored **at 150 °C**



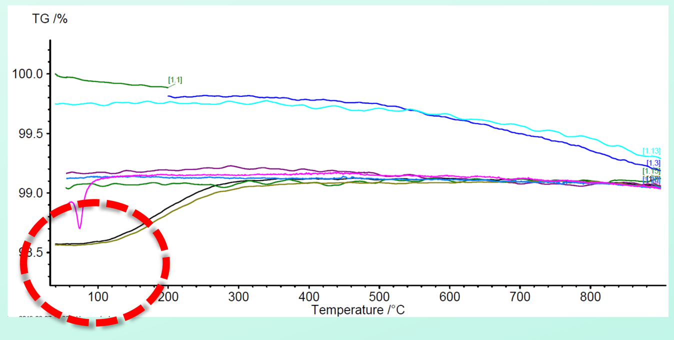


- *In situ* XRD (X-ray source: Mo K_α) confirmed reversibility and different peak broadening behaviour at 100 °C





Case 3. (La,Ca)(Fe,Co)$O_{3-\delta}$ nanoparticles at *even lower than* 100 °C

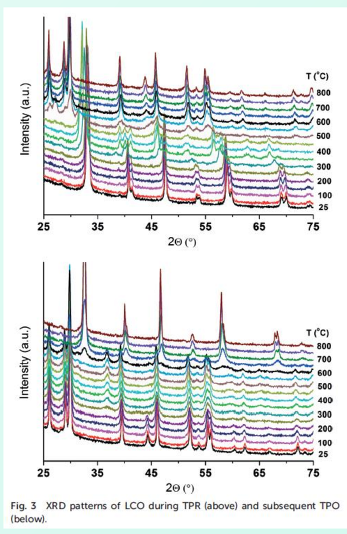


- Thermogravimetric analysis confirmed the entirely reversible, regenerative oxygen loss and uptake **at *even lower than* 100 °C**

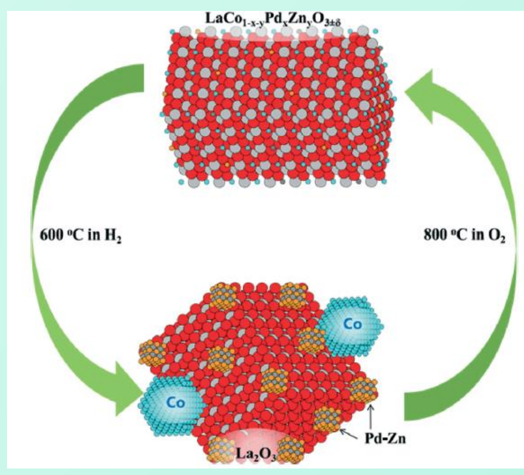
→ opens up new possibilities for reversible & regenerative chemical reactions **at room-temperature**

IV. Exsolutions during reversible redox reactions

Case 1. Exsoluted Pd-Zn in $La(Co_{1-x-y}Pd_xZn_y)O_{3\pm\delta}$ as methanol steam reforming catalysts – H_2 production



By *in situ* XRD, it is confirmed
- reduction begins only above 275 °C
- formation of vacancy-ordered perovskite-related structures such as $La_2Co_2O_5$ and $La_3Co_3O_8$ observed between 325 and 475 °C.
- complete reduction of the non rare-earth metal ions is attained between 550 and 625 °C.
- the single phase perovskite are completely restored above 700 °C

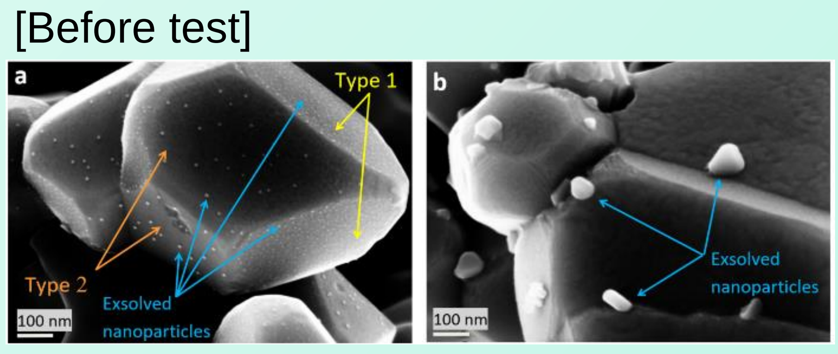


– Regenerative exsolution of Pd–Zn nanoparticles play crucial role in the low-temperature CO_2 selectivity

Kuc, Weidenkaff et al. *Catal. Sci. Technol.* **2016**, 6, 1455–1468

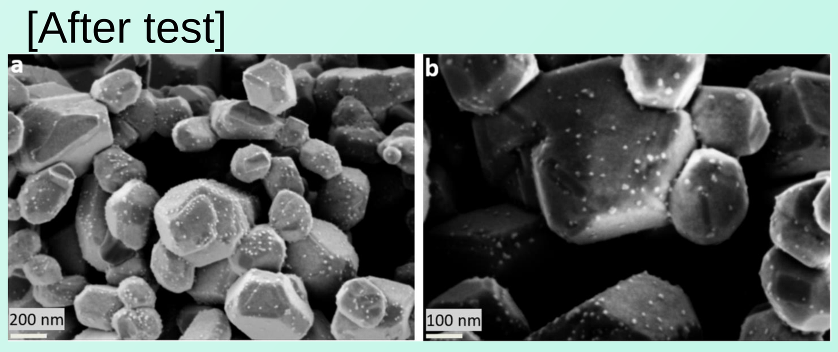
Case 2. Exsoluted Ni in $(La_{0.65}Sr_{0.30})(Cr_{0.85}Ni_{0.15})O_{3-\delta}$ as a fuel electrode for solid oxide cells (SOCs) – H_2 production

[Before test]



- SEM images of Ni exsolution on the surface of the perovskites after 3 hours treatment under H_2 atmosphere at (a) 500 °C and (b) 900 °C.
- Strongly correlated with the formation of oxygen vacancies, since the exsolution is favored when these oxygen vacancies reach a high concentration

[After test]



- SEM images with Ni nanoparticles after 950 hours co-electrolysis operation (co-EC) with the fuel gas composition of 5 % H_2, 63.7 % H_2O and 31.3 % CO_2 at 860 °C and -0.46 A•cm^{-2}
- This significant morphological change of Ni nanoparticles under operating conditions could affect their catalytic activities over time and thus impact the overall performance and durability of an electrode made of these materials.

Ni nanoparticle coarsening was limited, and the size of the exsolved nanoparticles increases until a critical stable radius under given test conditions of time and temperature

Amaya-Duenas, Weidenkaff et al. *J. Mater. Chem. A*, **2021**, Advance Article

V. Summary

Element specific (first-row transition elements: Mn, Fe, Co, Ni, and Zn) oxygen redox activity was presented thanks to the compositional flexibility and profound structural tolerance in perovskite oxides. A key issue addressed here is to show the feasibility of regenerative and reversible chemical reactions by an appropriate choice of the *A* and *B* elements in perovskite $ABO_{3-\delta}$ for many desirable applications in terms of energy production and conversion. As an outlook, IWKS will continue on the journey to realize the innovative synthesis and processing approaches to handle activity and stability issues keeping careful consideration for resource efficiency.

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