

Local effects in vanadia-based compounds

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■ Introduction

The current study, focuses on the temperature-dependent structural modulation of the local environment of M^{2+} ions in vanadium pentoxide (V_2O_5) and vanadates $Mn_xO-V_2O_5$.

The growing interest in V_2O_5 -based materials is in view of their potential for cathodes in M ion batteries [1].

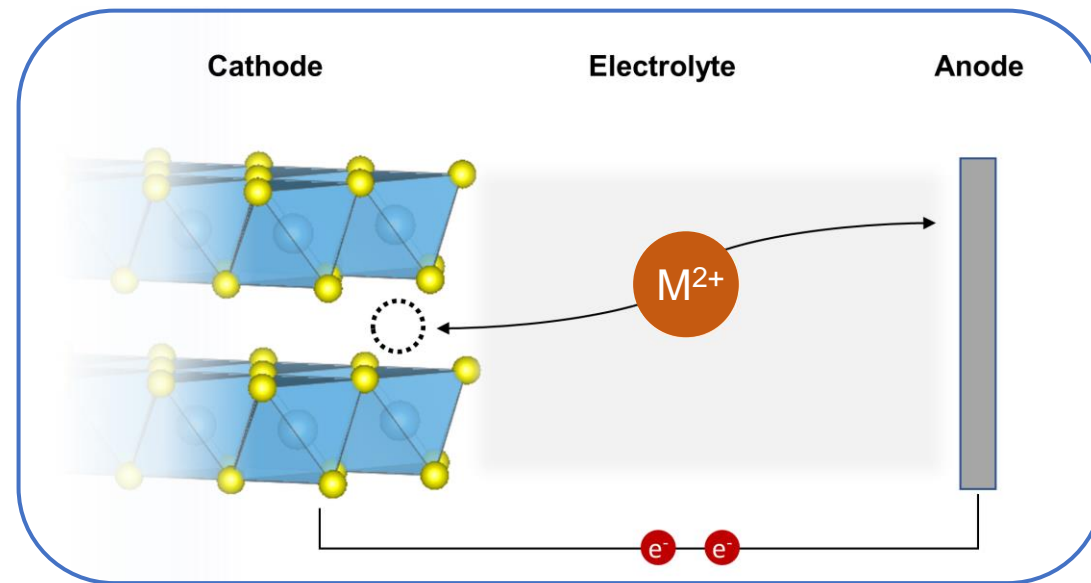


Figure 1 – Illustration of multivalent ion insertion in battery cathodes, adapter from [2]

■ Motivation

The (de)intercalation mechanism of M ions is considered fundamental to charge transfer [3], a detailed description of this process is still lacking.

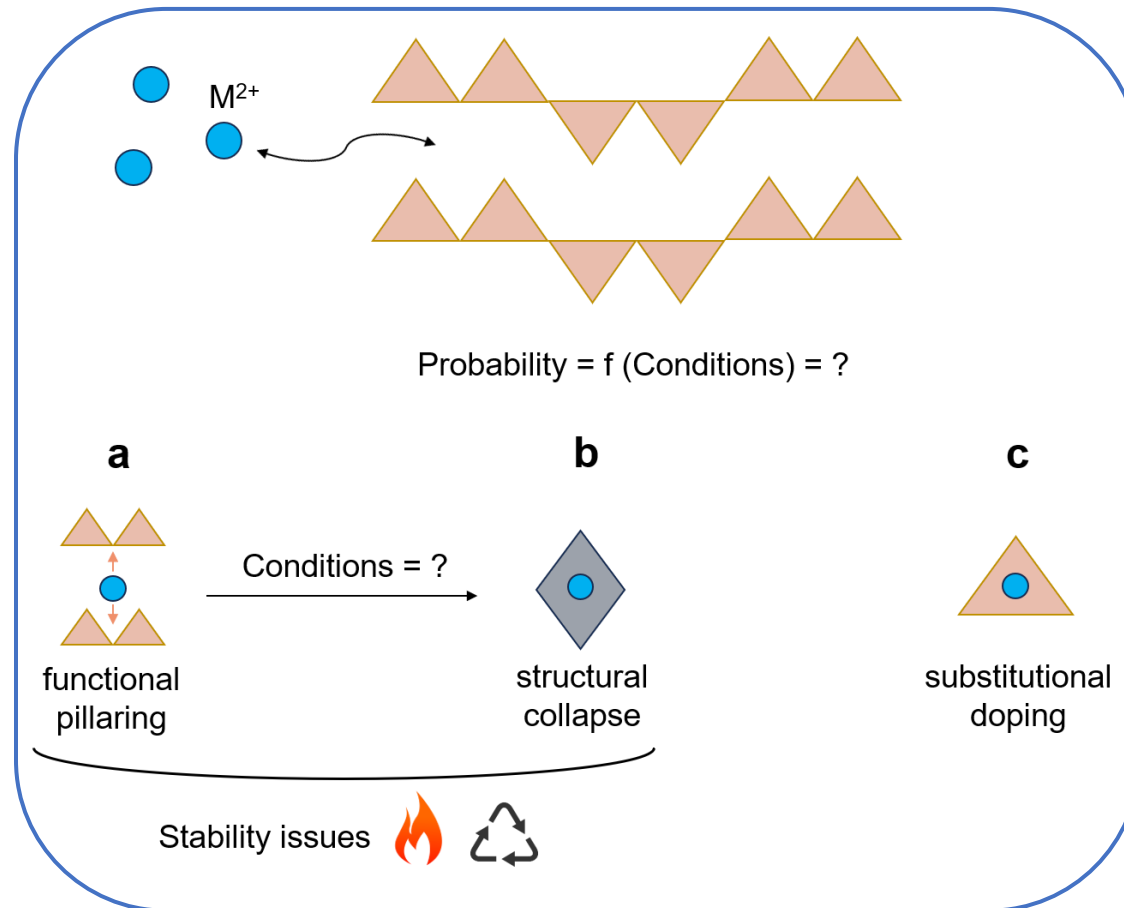


Figure 2 – Intercalation mystery for multivalent ions in batteries

■ Methods: synthesis

V_2O_5 :Cd samples were produced via wet impregnation of $^{111}\text{InCl}_3 \cdot \text{H}_2\text{O}$ (IPEN) into commercial V_2O_5 (>98% purity) and a consequent $^{111}\text{In} \rightarrow ^{111}\text{Cd}$ decay.

$\text{Mn}_x\text{O}-V_2\text{O}_5$:Cd were either prepared in similar manner at IPEN or obtained via ^{111m}Cd implantation at ISOLDE.

$\text{Mn}_x\text{O}-V_2\text{O}_5$ ($x=1, 2$) vanadates were synthesized using the standard Pechini route.

The X-ray diffraction method was employed to control over sample quality.

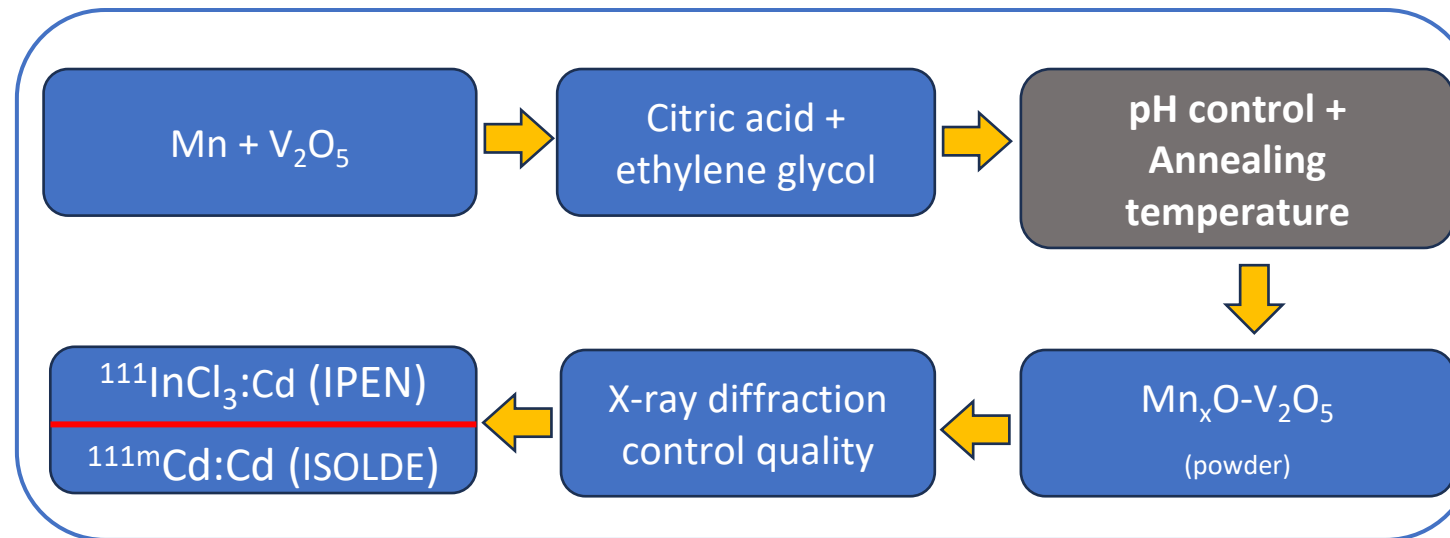


Figure 3 – Simplified synthesis process

■ Methods: TDPAC

Time Differential Perturbed Angular Correlation spectroscopy (TDPAC) is a hyperfine interactions, based method allowing the study of local effects and structure at atomic sites in molecules and materials.

Time and direction of emissions are recorded to extract information on the hyperfine split and, consequently, the environment of the probe nucleus.

These may be expressed in terms of Absolute value of the main component of electric field gradient tensor $|V_{zz}|$ and asymmetry parameter η .

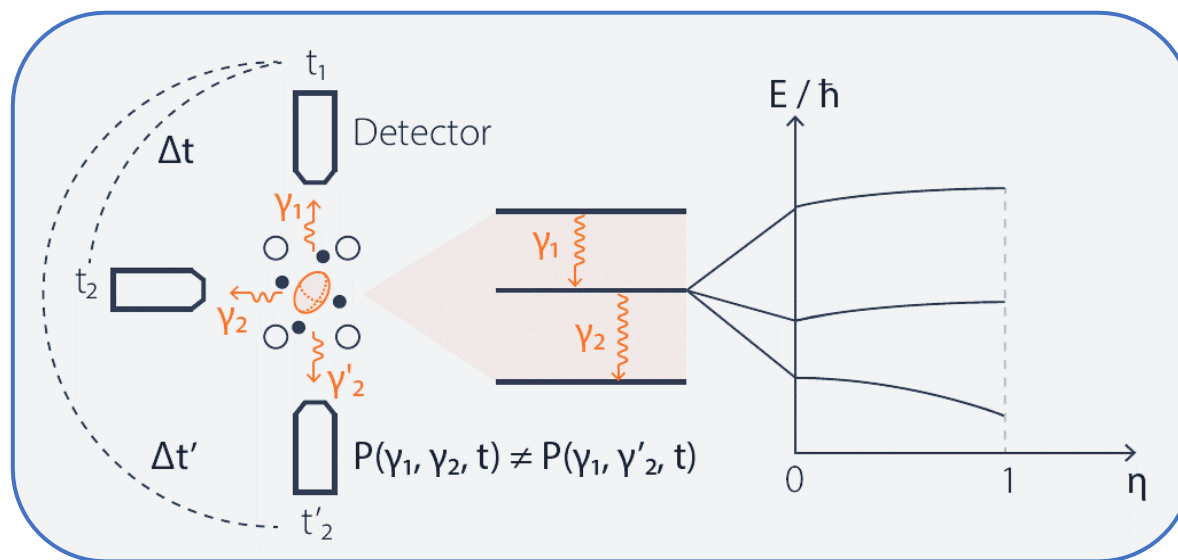


Figure 4 – Basic scheme for TDPAC experiment

Results

V₂O₅:Cd - IPEN

- The inset shows the decrease in V_{zz} broadening δ upon heating and Fourier transforms.
- The probe environment relaxes and regularizes

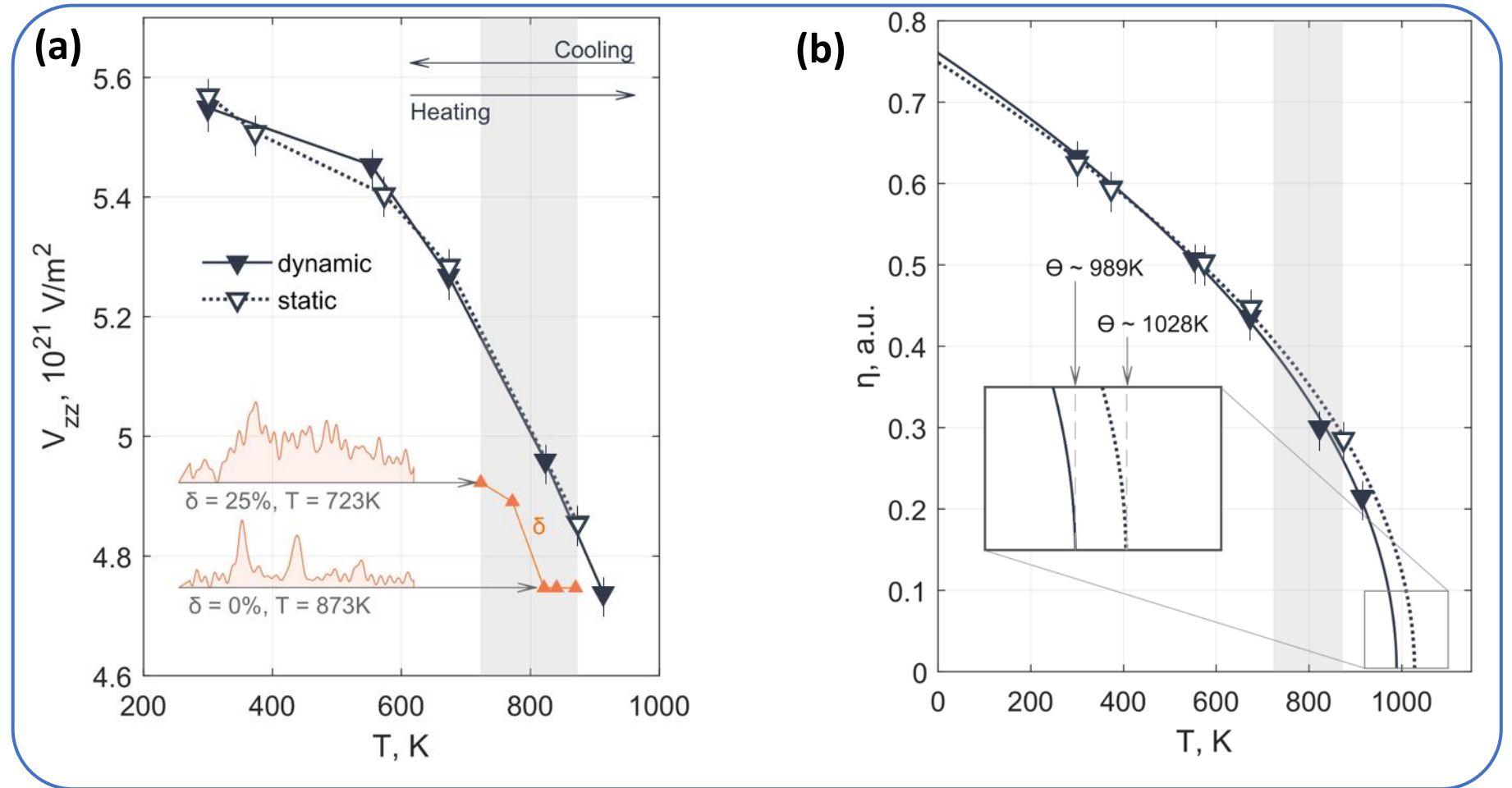


Figure 5 - (a) Evolution of the absolute value of V_{zz} upon cooling for the samples treated in static and dynamic vacuum. (b) Variation of asymmetry η upon cooling in static and dynamic vacuum and calculated approximations of the form $\eta(T) = \eta_0(1 - T/\Theta)^{1/2}$

Results

Mn_xO-V₂O₅:Cd – IPEN/ISOLDE

- The change is drastic from metavanadates
- This could be an indication of local ordering

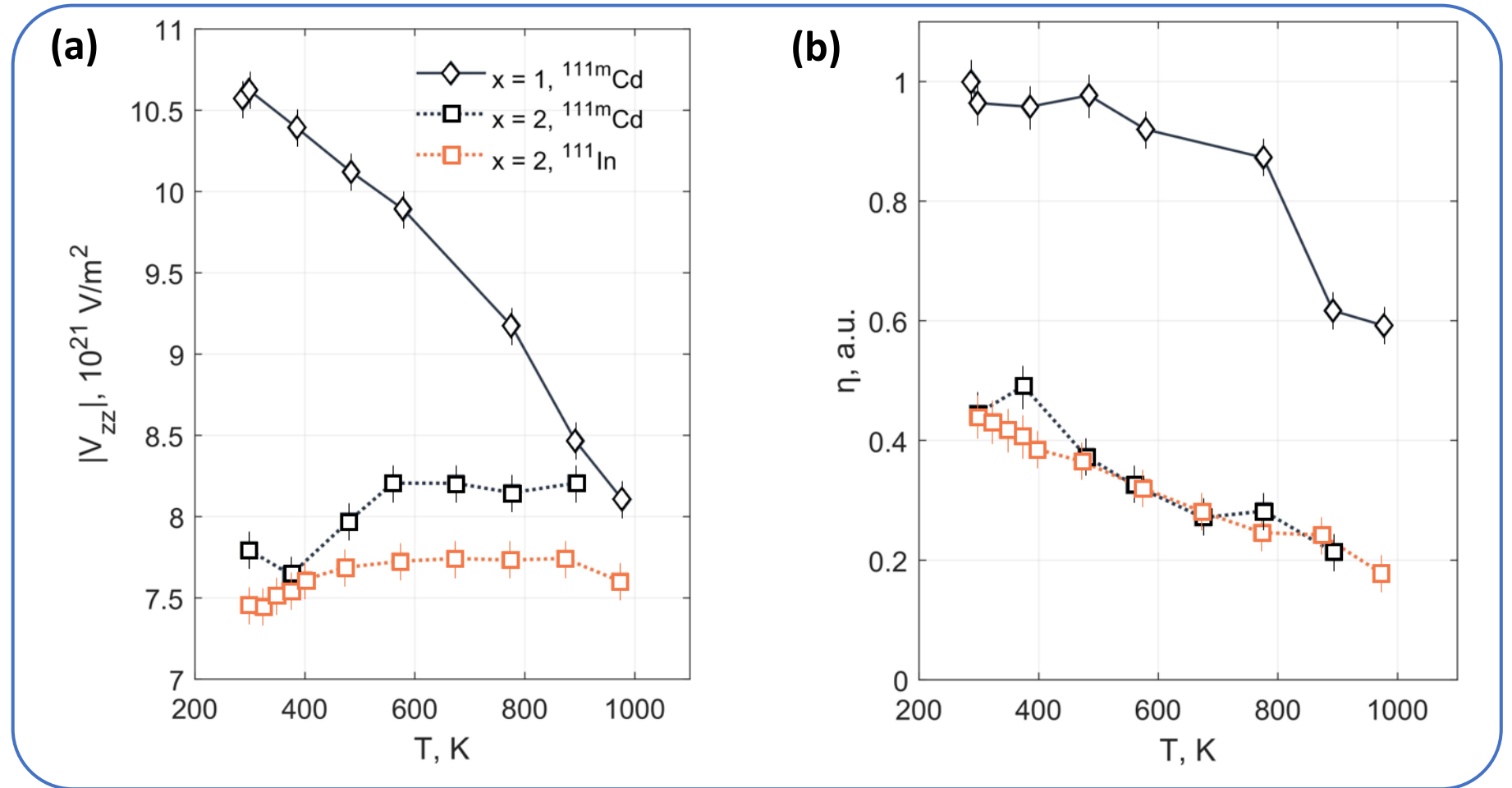


Figure 6 - (a) Temperature dependences of V_{zz} , (b) η obtained with different probe parents (¹¹¹mCd and ¹¹¹In) in nominal Mn_x-V₂O₅ meta (x=1) and pyrovanadates (x=2)

■ Summary

- ❖ The behavior of hyperfine parameters indicates a temperature-dependent modulation of the local environment of the Cd probes in both V_2O_5 :Cd and Mn_xO - V_2O_5 :Cd systems.
- ❖ The observed effect can be associated to either distortions:
 - induce by the probe
 - intrinsic local structural variation
- ❖ Meanwhile, care must be taken to distinguish between local distortions induced by the probe and structure variations.

■ Perspectives

With the help of obtained theoretical tools, we intend to understand the paths of hyperfine parameters across temperature variations and attribute those to structural relaxations previously observed with XRD and currently mapped with TDPAC for vanadates.

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■ References

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