Cadmium doping in vanadium oxides and Cadmium vanadates investigated by hyperfine interactions at ^{111m}Cd probe nuclei

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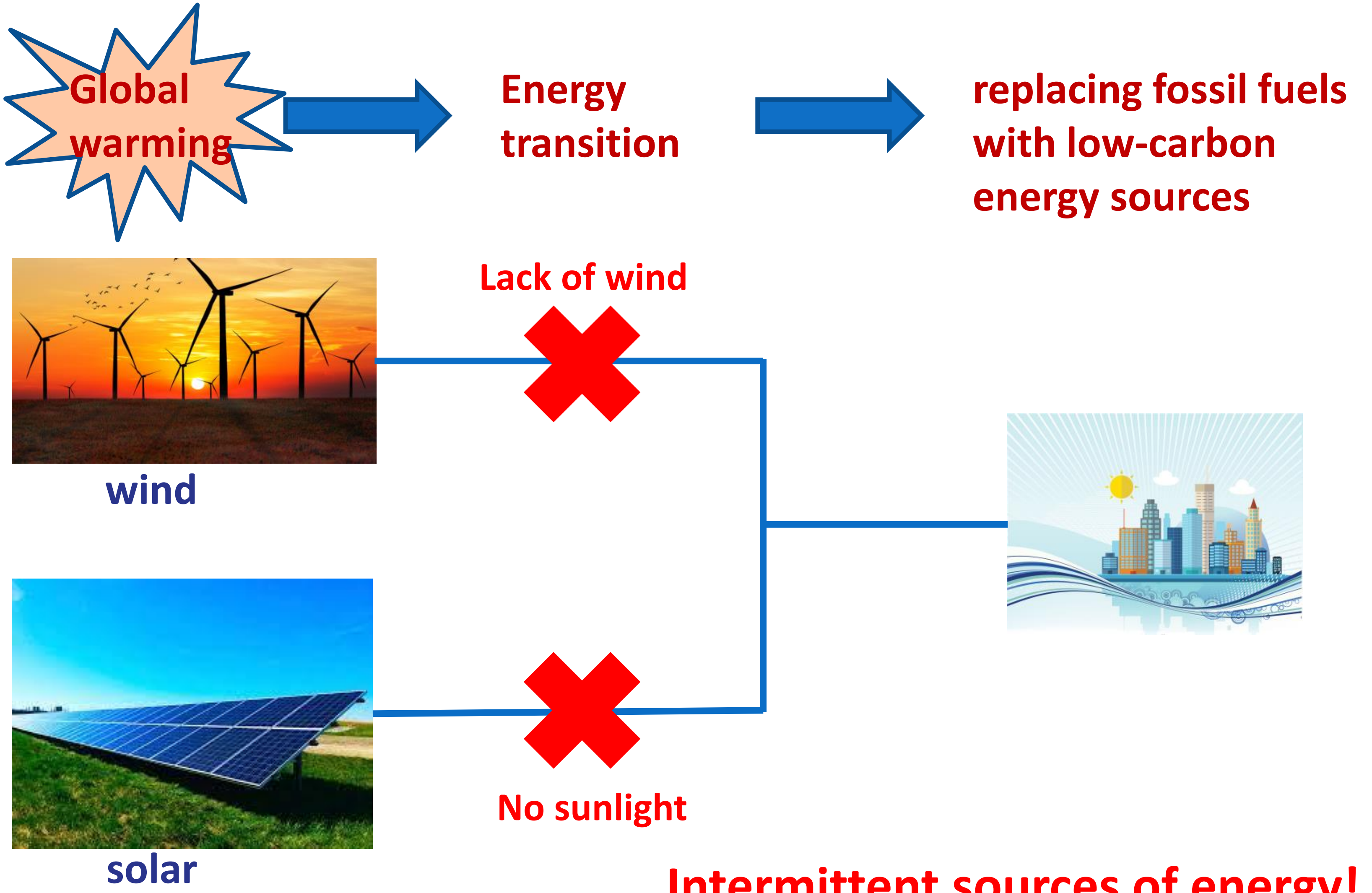
Motivation

Global warming → Energy transition → replacing fossil fuels with low-carbon energy sources

wind

solar

Motivation

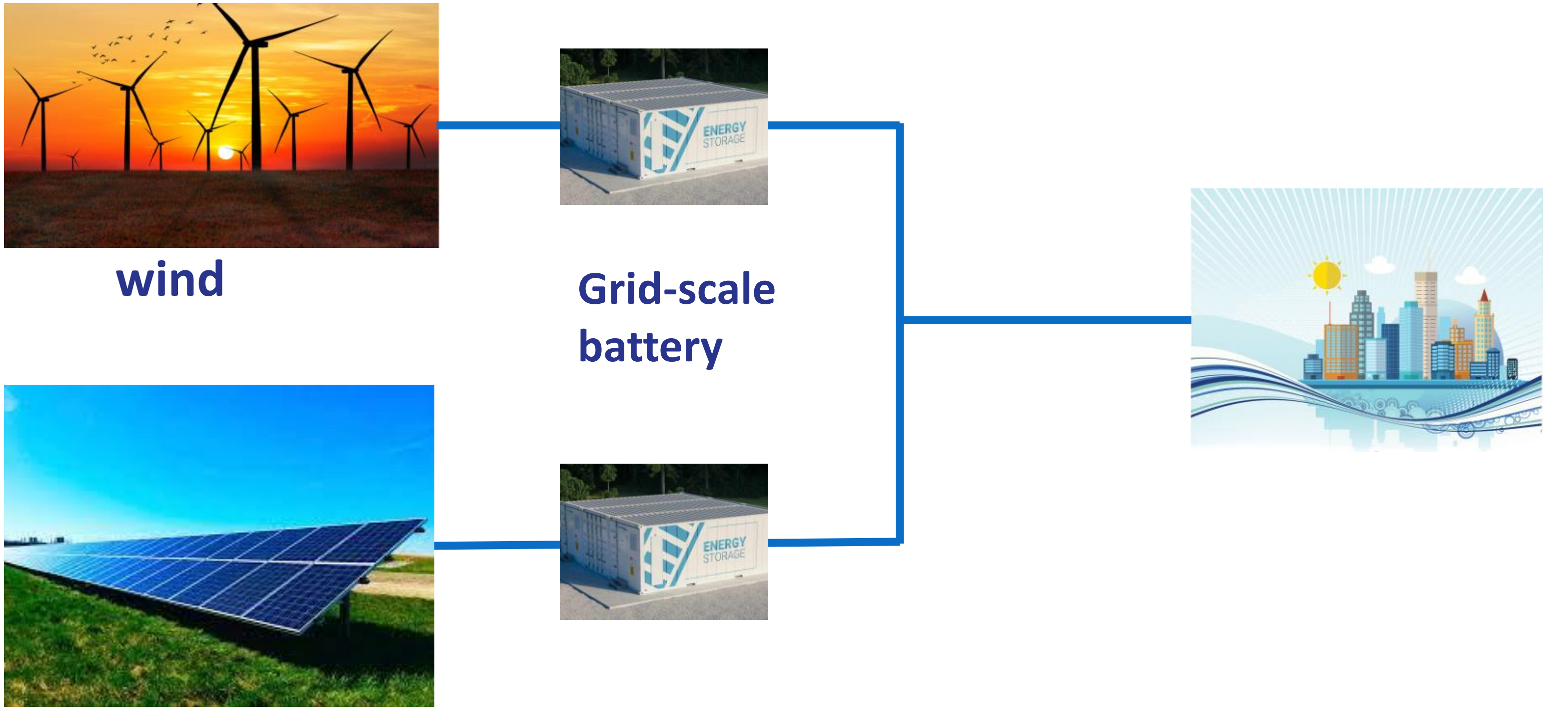


Global warming → Energy transition → replacing fossil fuels with low-carbon energy sources

Intermittent sources of energy!

Motivation

Global warming → Energy transition → replacing fossil fuels with low-carbon energy sources



wind

Grid-scale battery

solar

Solution: save energy in batteries!

Grid-scale batteries

Li-ion batteries (LIB) currently dominate but face scaling challenges for grid-level storage.

Aqueous rechargeable batteries, specifically zinc-ion batteries (AZIB), are promising devices for addressing the grid-scale energy storage issue.

LIB

- high cost
- Limited Li resources
- Toxicity
- Safety (explosion)
- lifespan

AZIB

- Low cost
- environmentally friendly
- safe
- Long-term cycles
- Nontoxicity
- High Zn anode capacity
- higher ionic conductivities

Because of the small ionic radii of Zn^{2+} (0.74 Å), tunnel-type and layered-type structures allow for the insertion/extraction of Zn^{2+} ions into/from their hosts.

Cathode

Because **electrode materials** are an important component of battery-based systems, the electrochemical performance of batteries is strongly influenced by their characteristics

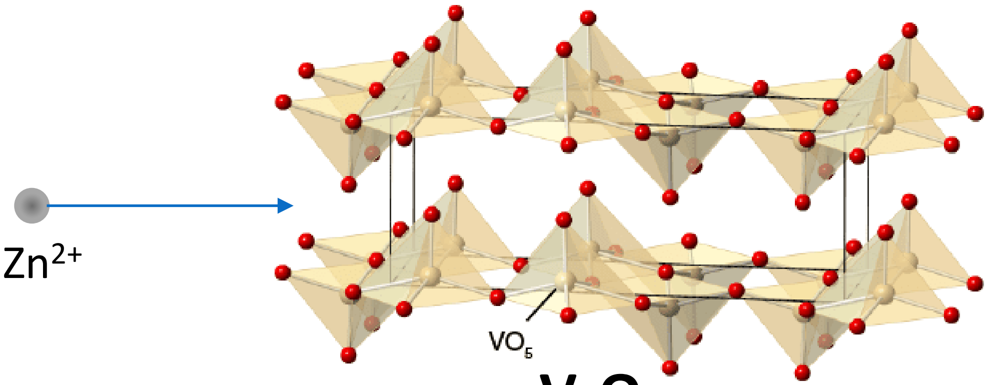
Vanadium-based materials in particular offer promising potential for producing battery electrodes due to:

- high specific capacity,
- remarkable stability,
- low cost.

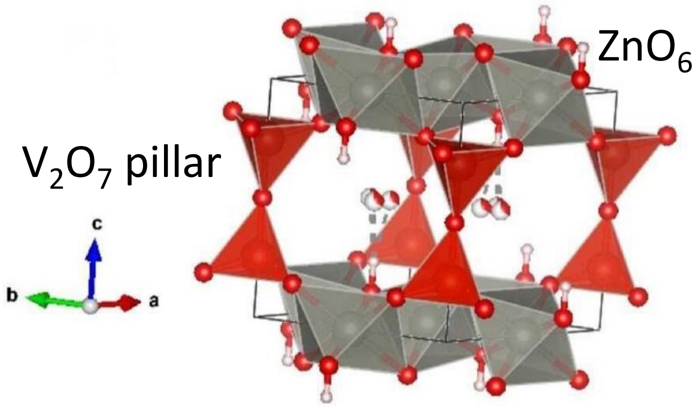
The good properties of vanadium-based compounds are due to the wide range of oxidation states (*i.e.* +2 to +5) that vanadium can adopt, as well as the impressive diversity of crystalline structure.

Vanadium oxide structure

Advantage of V_2O_5: layered structure

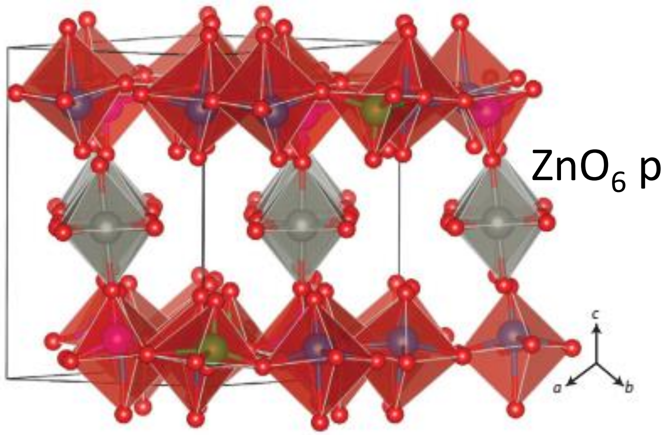


V_2O_5



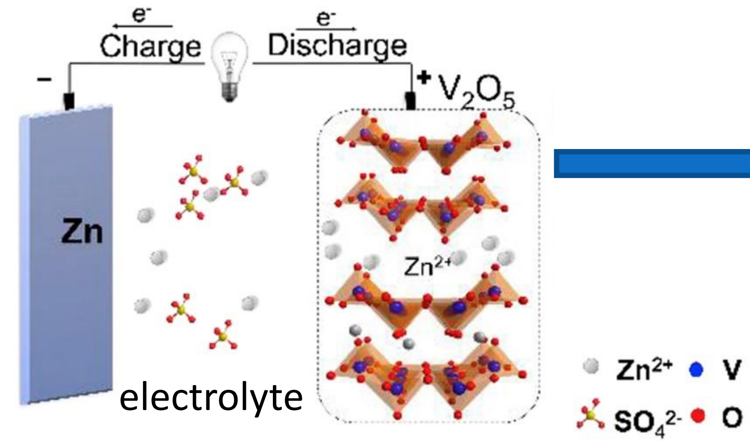
$Zn_3V_2O_7(OH)_2\cdot 2H_2O$

Zinc vanadate

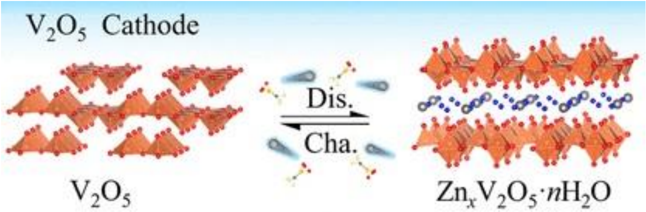


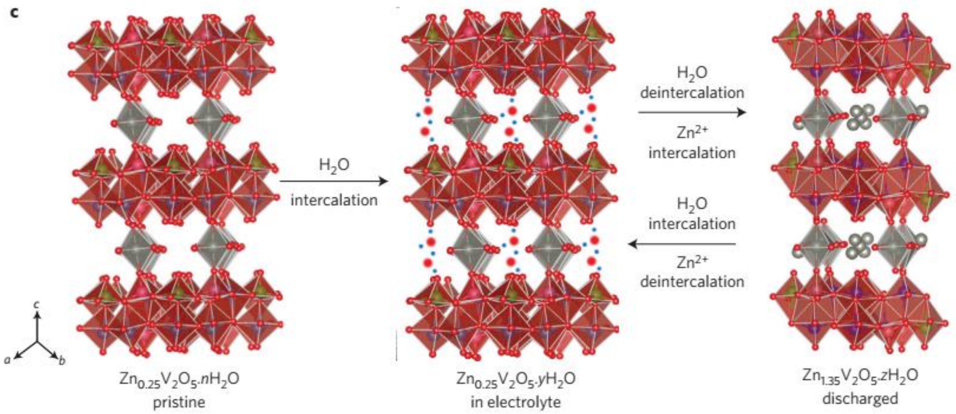
Zn-doped V_2O_5

V-based cathode battery



anode cathode





Unsolved issues

The processes that take place in AZIB systems are complex and controversial. Numerous issues are still undeveloped and up for debate.

The reaction mechanisms in AZIB systems are complicated and debatable,

Zn^{2+} insertion/extraction processes,

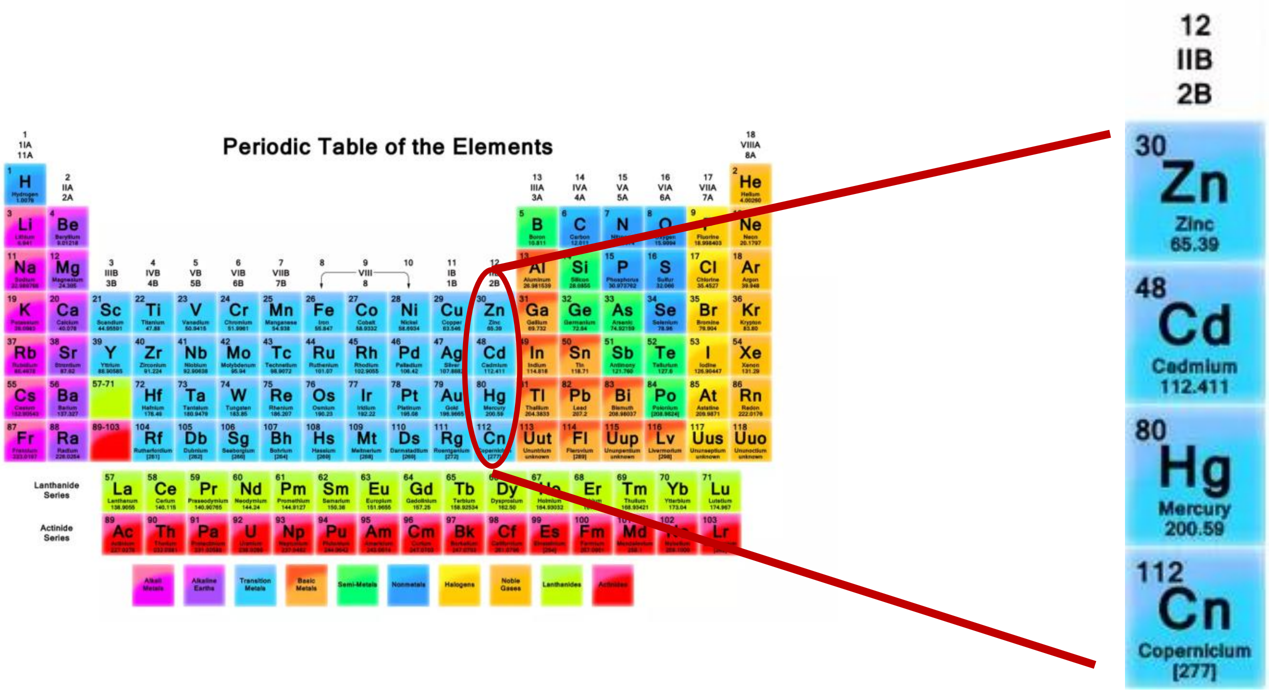
Charge transfer mechanism of the divalent ions,

Structural stability of layered type vanadates upon repeated cycling,

Engineering the structural interlayer can increase the Zn2+ host capacity and the intrinsic ionic conductivity,

Electrochemical performance of batteries is closely related to the properties of the electrode.

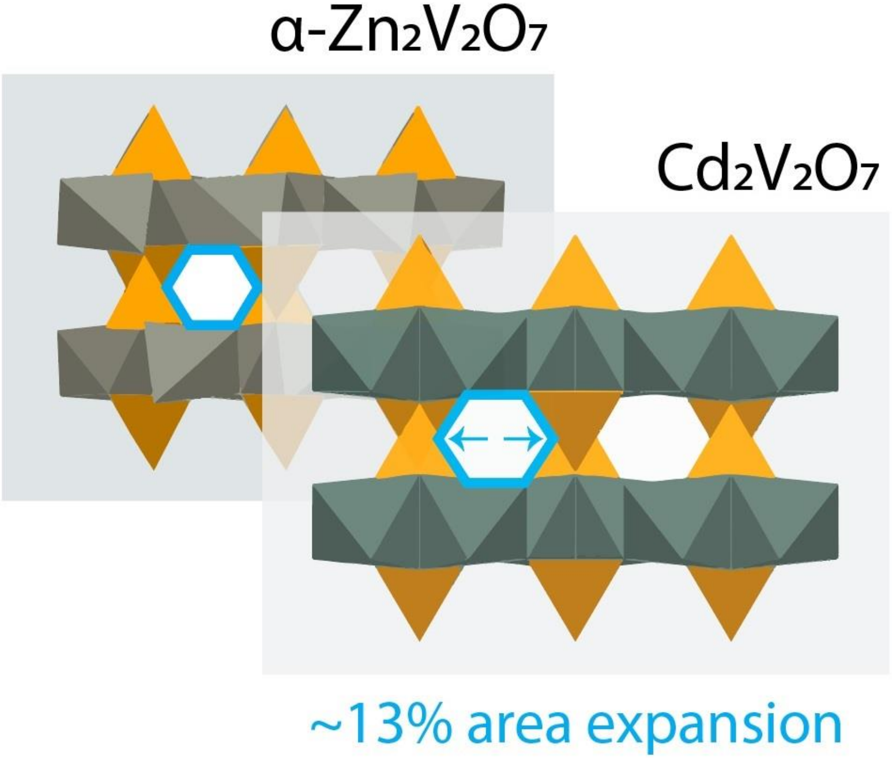
Objectives



Cadmium's ionic radius is 24% greater than zinc's.

Cadmium may replace Zinc in doped V_2O_5 or vanadates increasing the electrochemical performance

Objectives



Investigation of Cd-doped V_2O_5 and Cd vanadates, experimentally by TDPAC and theoretically by first-principles calculations.

Samples and sample preparation

We have measured four categories of samples:

A. Vanadium pentaoxide (V_2O_5) samples were two types:
i) Commercial (COM) oxide (Alfa Aesar 99.999%),
ii) sol-gel (SG) prepared from pure V

B. Vanadium pentaoxide doped with Cd (1%, 5%, and 10%)

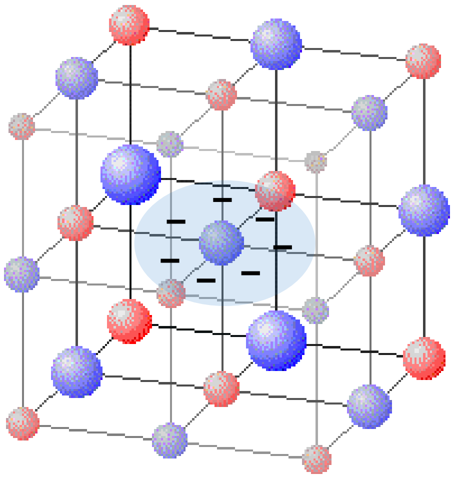
i) Sol-gel prepared from pure elements V and Cd

C. Cd vanadates (CdV_2O_6 and $Cd_2V_2O_7$)
i) Sol-gel prepared form pure elements V and Cd

D. Vanadium dioxide (VO_2)
i) Hydrothermally prepared (HT) VO_2
ii) Commercial VO_2
iii) Thin film VO_2 on Al_2O_3 substrates

Hyperfine Interactions (HFI)

Electric Interaction



Electron charge density

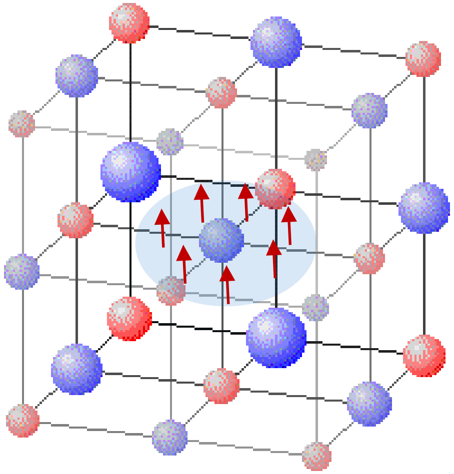
↓

Electric field Gradient (V_{ii})

⇅ **HFI**

Nuclear quadrupole moment

Magnetic Interaction



Electron spin density

↓

Magnetic field (B_{hf})

HFI ⇅

Nuclear dipole magnetic moment

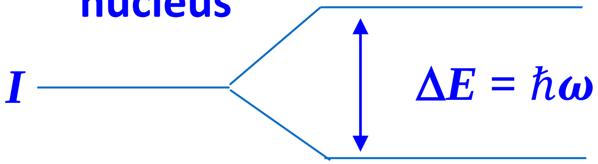
Nuclear quadrupole moment ⇐ **Probe nucleus** ⇒ **Nuclear dipole magnetic moment**

Perturbed angular correlation

Electric Interaction

Magnetic Interaction

Probe nucleus



Nuclear state I

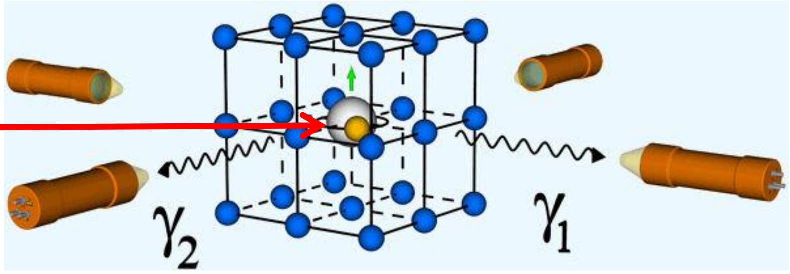
$\Delta E = \hbar\omega$

$$\omega_Q = \frac{eQV_{zz}}{4I(2I-1)\hbar}$$

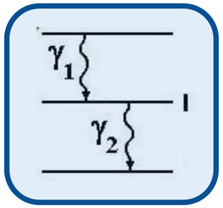
$$\omega_L = g_N \mu_N \frac{B_{hf}}{\hbar}$$

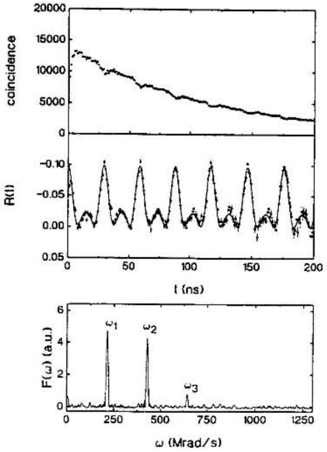
$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}}$$

Perturbed Angular Correlation (PAC)



Radioactive probe nucleus





RESULTS

We have tried different **annealing after implantation**, including no annealing (as implanted).

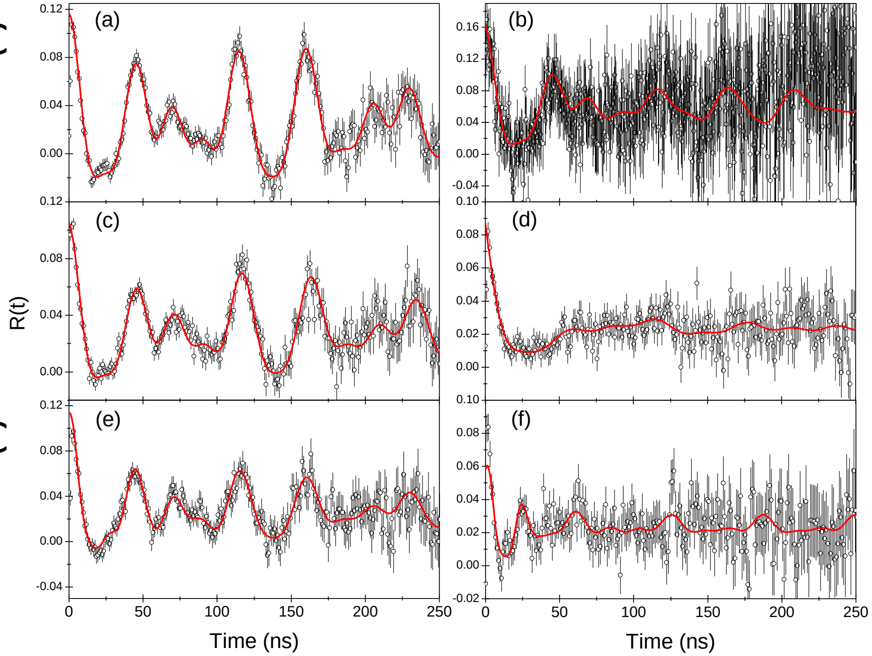
V_2O_5 samples were annealed in air, vacuum or a mix of both.

The best annealing was a mix of dynamic vacuum (**DV**) for 5 min, static vacuum (**SV**) for 5 min, followed by annealing in air for 5 min, hereafter called ***555 annealing***.

COM-555 at 500 °C

SG-555 at 570 °C

COM-555 at 570 °C



COM-AIR at 500 °C
for 20 min

SG-DV at 500 °C
for 20 min

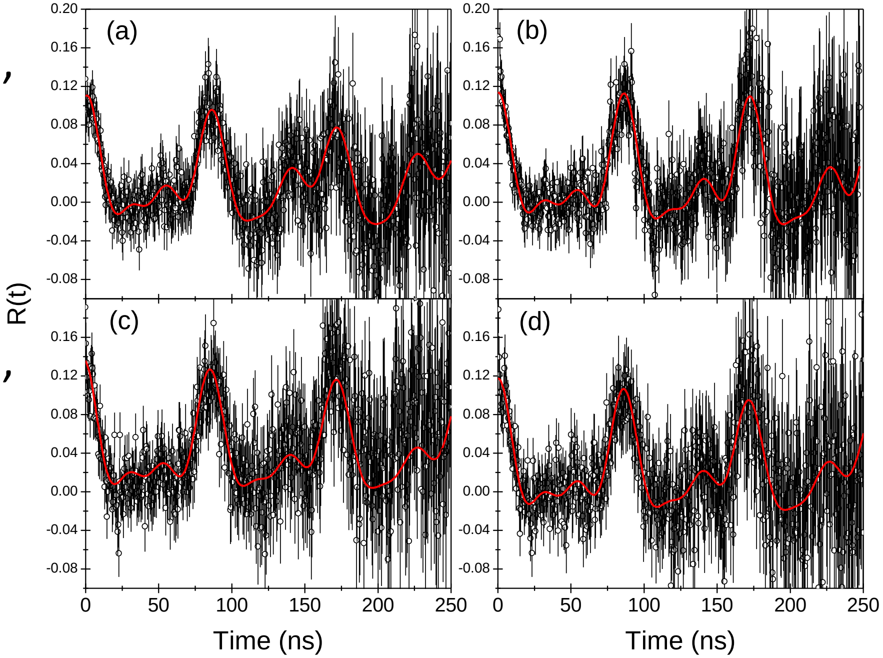
SG-AIR at 500 °C
for 20 min

Results

we tested the hypothesis of a thermal reduction of V_2O_5 to VO_2 (via annealing at 600 °C during evacuation)

COM sample, under SV

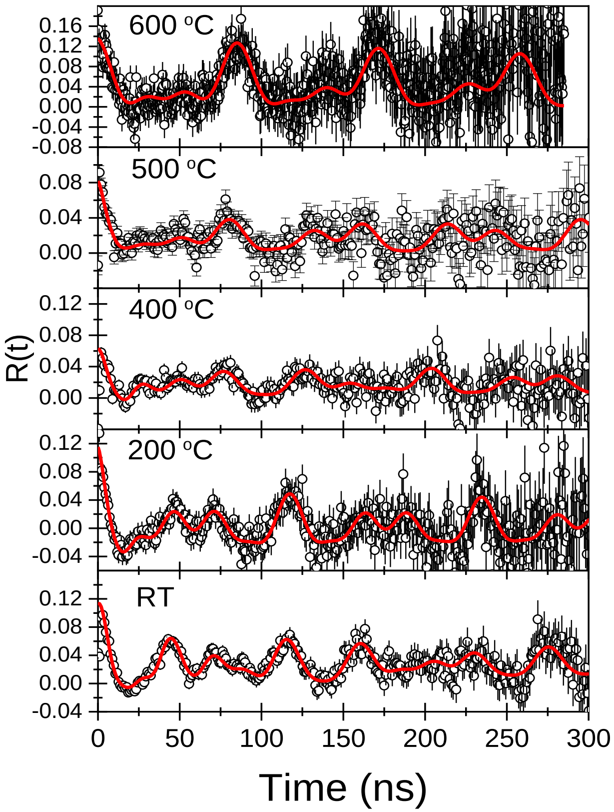
COM sample, in AIR



COM sample, under DV

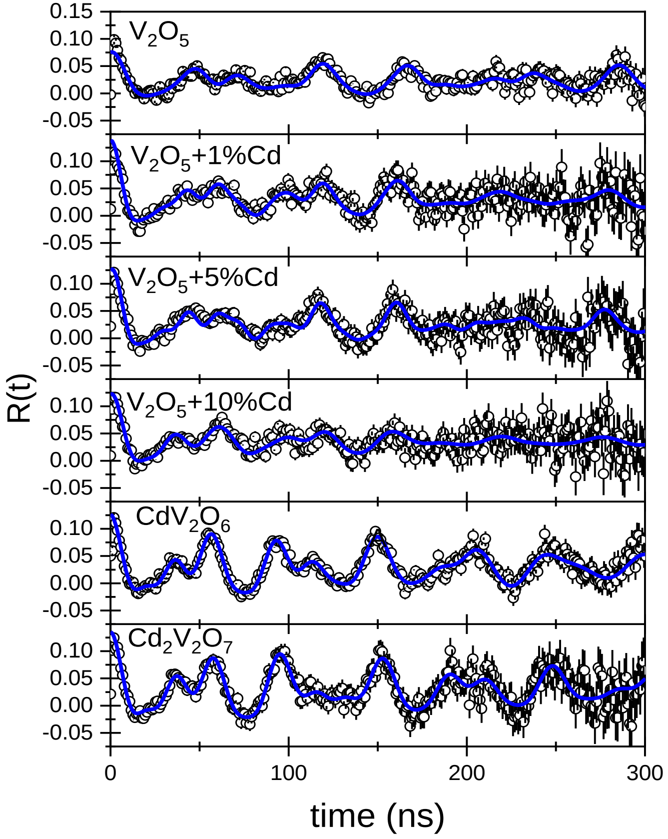
SG sample, in AIR

Results



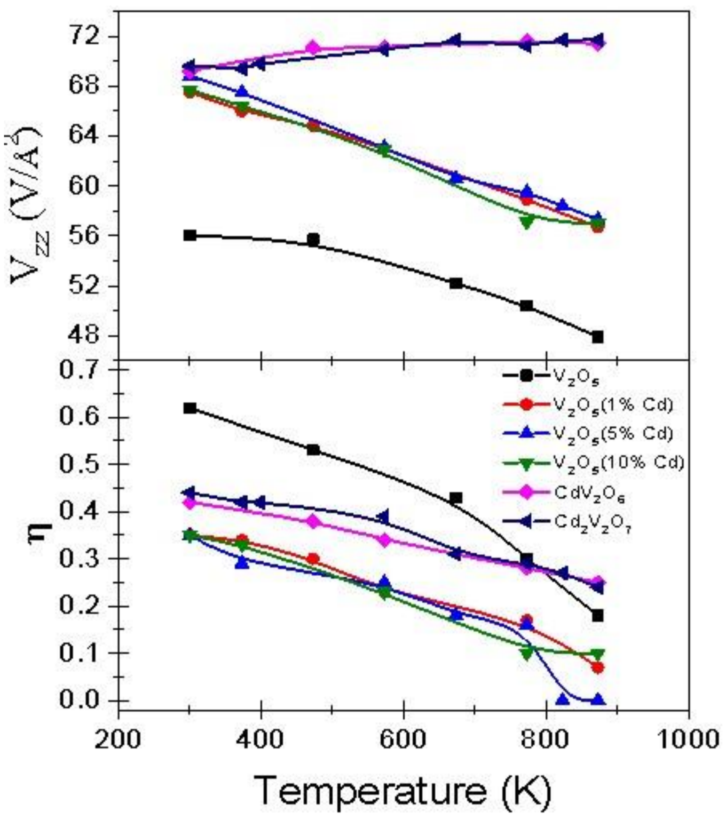
V_2O_5 COM samples measured at different temperatures in AIR

Results



Cd-doped V_2O_5 and Cd vanadates compared with V_2O_5 sample measured at RT

Results and Discussion



Values of Vzz for Cd-doped V_2O_5 and for V_2O_5 decrease when temperature increases.

Vzz for vanadates is almost independent of temperature

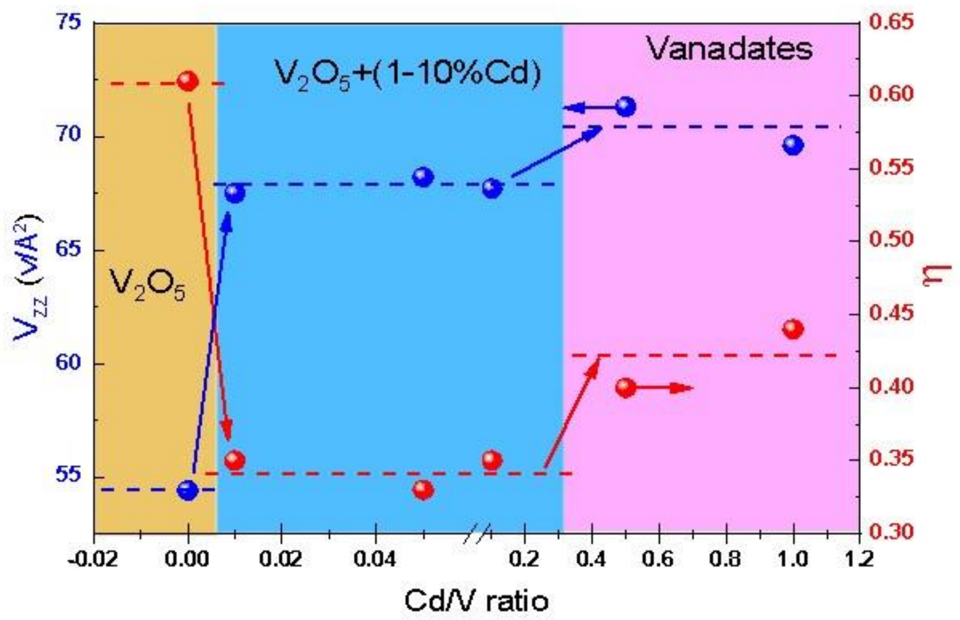
Values of η for Cd-doped V_2O_5 and for V_2O_5 decrease appreciably with temperature.

η for vanadates decreases less profoundly with temperature

It is an indication of a intense change in the charge density around the Cd

Cd vanadate is more stable with the increase of temperature

Results and Discussion



At RT, values of Vzz for Cd-doped V_2O_5 and vanadates are higher than that for V_2O_5

Values of η for Cd-doped V_2O_5 and vanadates are lower than that for V_2O_5

These differences may be ascribed to the interlayer structure

Next

First-principles calculations:

Are ^{111m}Cd probes replacing V atoms, or are they at interstitial sites?

Presence of oxygen vacancies?

Investigation by PAC of Zn vanadates and Zn-doped V_2O_5