



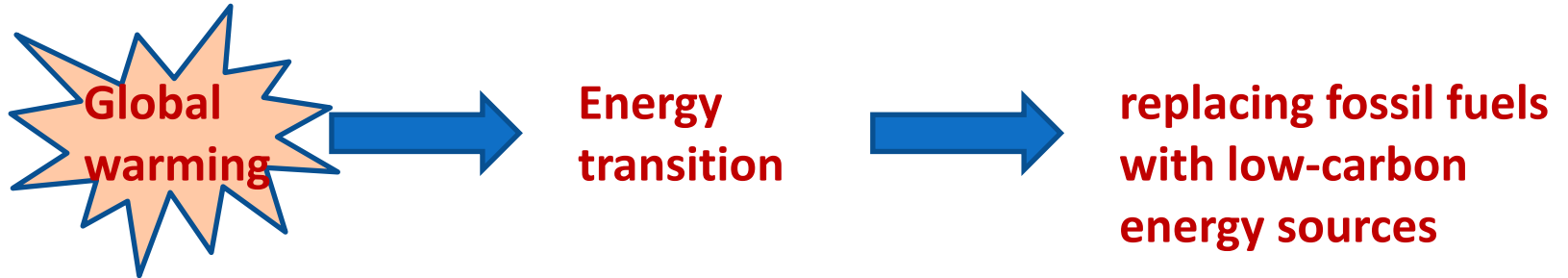
Cadmium doping in vanadium oxides and Cadmium vanadates investigated by hyperfine interactions at ^{111m}Cd probe nuclei

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Motivation



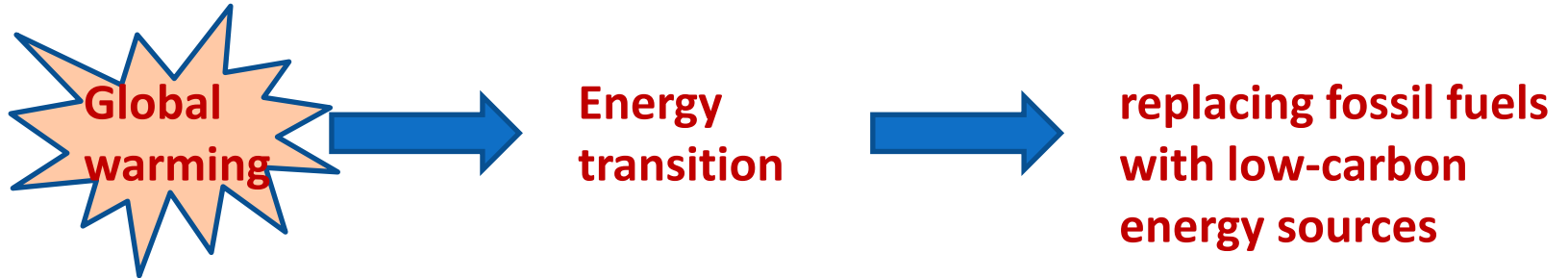
wind



solar



Motivation



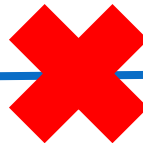
wind

Lack of wind



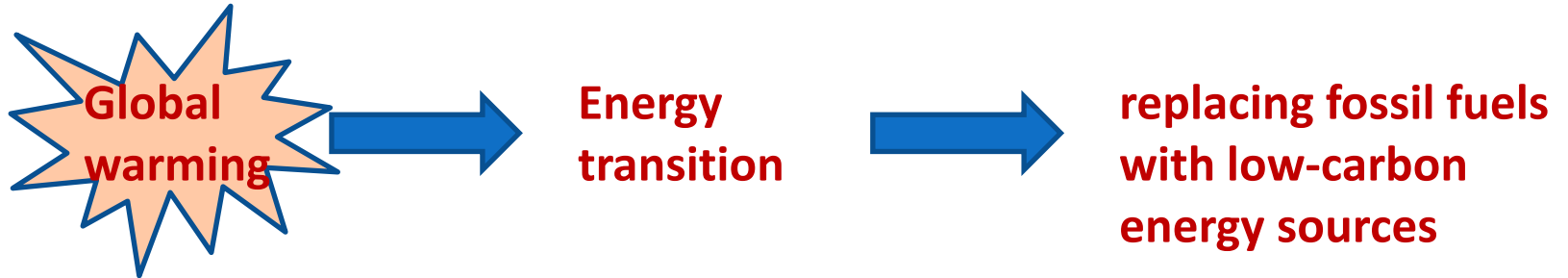
solar

No sunlight



Intermittent sources of energy!

Motivation



wind



solar



Grid-scale battery



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

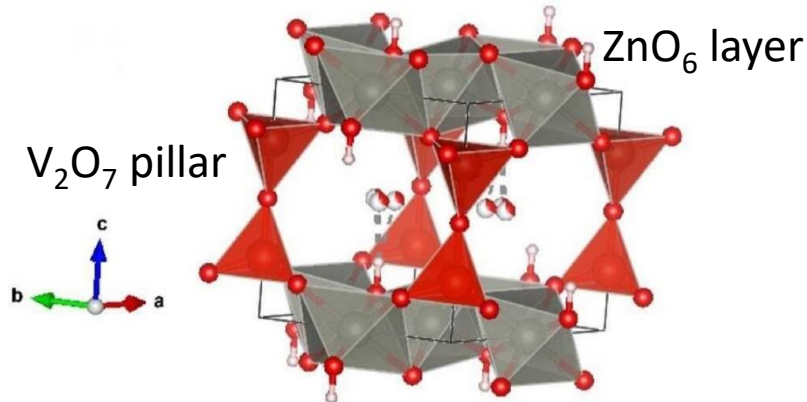
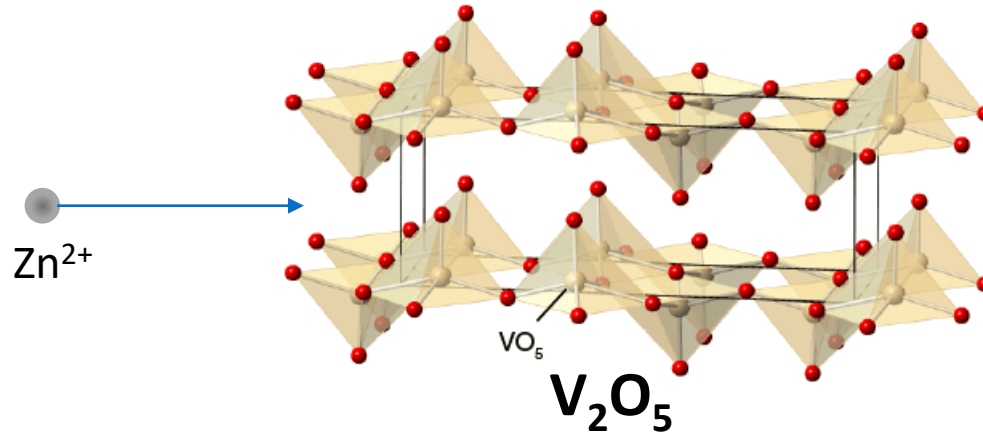
Vanadium-based materials in particular offer promising potential for producing battery electrodes due to:

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

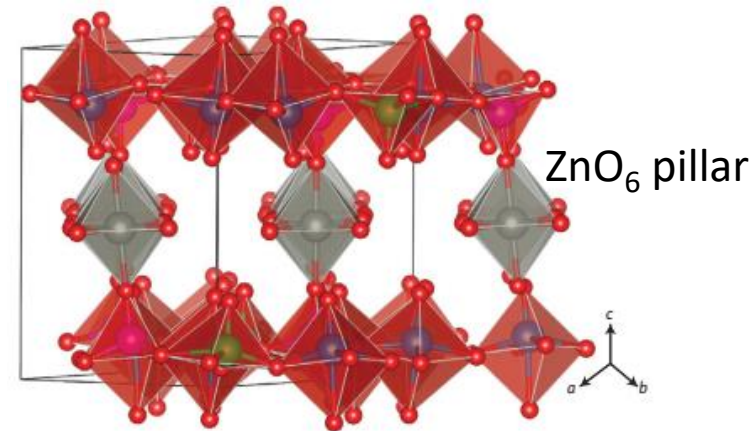
The good properties of vanadium-based compounds are due to the wide range of oxidation states (*i.e.* +2 to +5) that vanadium can adopt, as well as the impressive diversity of crystalline structure.

Vanadium oxide structure

Advantage of V_2O_5 : layered structure

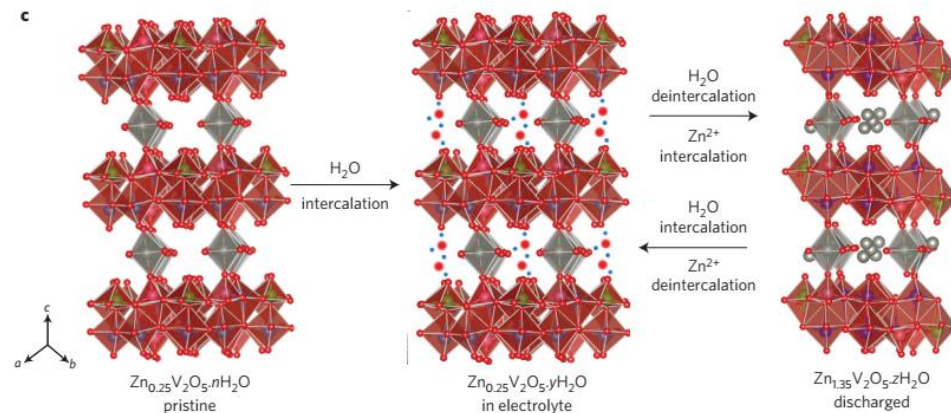
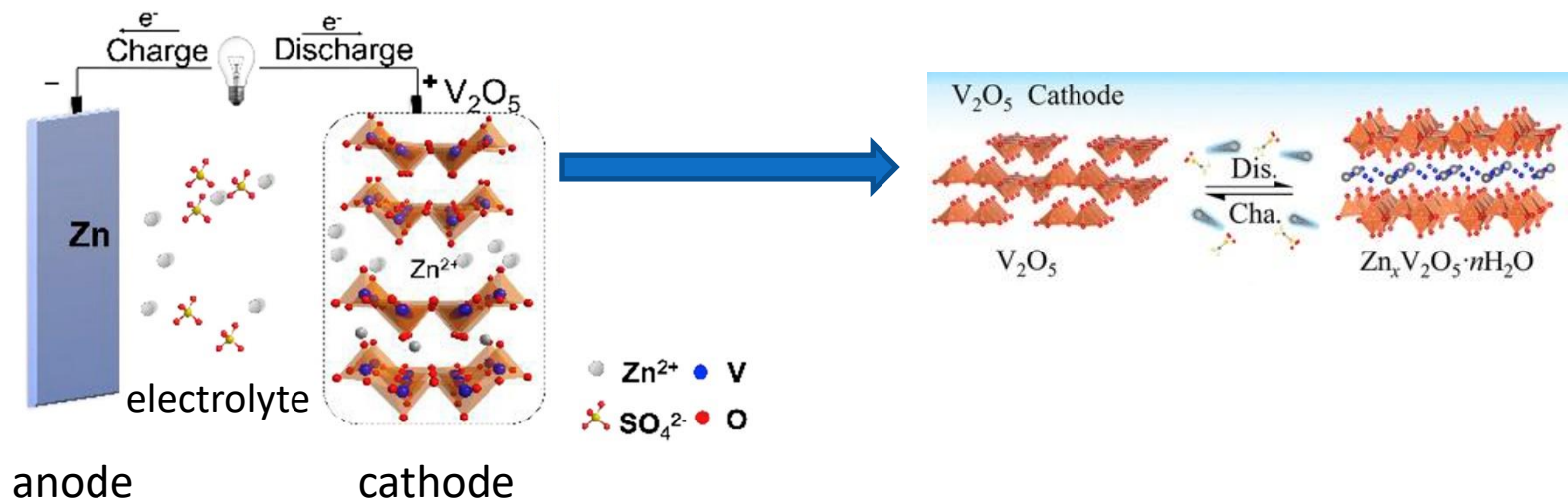


$Zn_3V_2O_7(OH)_2 \cdot 2H_2O$
Zinc vanadate



Zn-doped V_2O_5

V-based cathode battery



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,

Zn²⁺ 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

Periodic Table of the Elements

| | | | | | | | | | | | | | | | | | |
|--|---|--------------------------------|-------------------------------------|---------------------------------|----------------------------------|----------------------------------|---------------------------------|----------------------------------|------------------------------------|-----------------------------------|-----------------------------------|--|--|---|---|---|--|
| 1 11A H Hydrogen 1.008 | 2 IIA 2A He Helium 4.003 | | | | | | | | | | | 13 IIIA 3A Al Aluminum 26.982 | 14 IVA 4A Si Silicon 28.086 | 15 VA 5A P Phosphorus 30.974 | 16 VIA 6A S Sulfur 32.06 | 17 VIIA 7A Cl Chlorine 35.45 | 18 VIIIA 8A Ar Argon 39.948 |
| 3 Li Lithium 6.941 | 4 Be Beryllium 9.012 | | | | | | | | | | | 5 B Boron 10.81 | 6 C Carbon 12.011 | 7 N Nitrogen 14.007 | 8 O Oxygen 15.999 | 9 F Fluorine 18.998 | 10 Ne Neon 20.180 |
| 11 Na Sodium 22.990 | 12 Mg Magnesium 24.305 | 13 Al Aluminum 26.982 | 14 Si Silicon 28.086 | 15 P Phosphorus 30.974 | 16 S Sulfur 32.06 | 17 Cl Chlorine 35.45 | 18 Ar Argon 39.948 | | | | | | | | | | |
| 19 K Potassium 39.098 | 20 Ca Calcium 40.078 | 21 Sc Scandium 44.956 | 22 Ti Titanium 47.88 | 23 V Vanadium 50.942 | 24 Cr Chromium 51.996 | 25 Mn Manganese 54.938 | 26 Fe Iron 55.845 | 27 Co Cobalt 58.933 | 28 Ni Nickel 58.693 | 29 Cu Copper 63.546 | 30 Zn Zinc 65.38 | 31 Ga Gallium 69.723 | 32 Ge Germanium 72.63 | 33 As Arsenic 74.922 | 34 Se Selenium 78.96 | 35 Br Bromine 79.904 | 36 Kr Krypton 83.8 |
| 37 Rb Rubidium 85.468 | 38 Sr Strontium 87.62 | 39 Y Yttrium 88.906 | 40 Zr Zirconium 91.224 | 41 Nb Niobium 92.906 | 42 Mo Molybdenum 95.94 | 43 Tc Technetium 98.906 | 44 Ru Ruthenium 101.07 | 45 Rh Rhodium 102.905 | 46 Pd Palladium 106.42 | 47 Ag Silver 107.868 | 48 Cd Cadmium 112.411 | 49 In Indium 114.818 | 50 Sn Tin 118.71 | 51 Sb Antimony 121.757 | 52 Te Tellurium 127.6 | 53 I Iodine 126.905 | 54 Xe Xenon 131.29 |
| 55 Cs Cesium 132.905 | 56 Ba Barium 137.327 | 57-71 Lanthanide Series | 72 Hf Hafnium 178.49 | 73 Ta Tantalum 180.948 | 74 W Tungsten 183.84 | 75 Re Rhenium 186.207 | 76 Os Osmium 190.23 | 77 Ir Iridium 192.225 | 78 Pt Platinum 195.084 | 79 Au Gold 196.967 | 80 Hg Mercury 200.59 | 81 Tl Thallium 204.383 | 82 Pb Lead 207.2 | 83 Bi Bismuth 208.980 | 84 Po Polonium 209 | 85 At Astatine 210 | 86 Rn Radon 222 |
| 87 Fr Francium [223] | 88 Ra Radium [226] | 89-103 Actinide Series | 104 Rf Rutherfordium [261] | 105 Db Dubnium [262] | 106 Sg Seaborgium [266] | 107 Bh Bohrium [264] | 108 Hs Hassium [277] | 109 Mt Meitnerium [268] | 110 Ds Darmstadtium [271] | 111 Rg Roentgenium [272] | 112 Cn Copernicium [285] | 113 Nh Nihonium [284] | 114 Fl Flerovium [289] | 115 Uup Ununpentium [288] | 116 Lv Livermorium [293] | 117 Uus Ununseptium [294] | 118 Uuo Ununoctium [294] |
| Legend: Alkali Metals, Alkaline Earths, Transition Metals, Basic Metals, Semi-Metals, Nonmetals, Halogens, Noble Gases, Lanthanides, Actinides | | | | | | | | | | | | | | | | | |

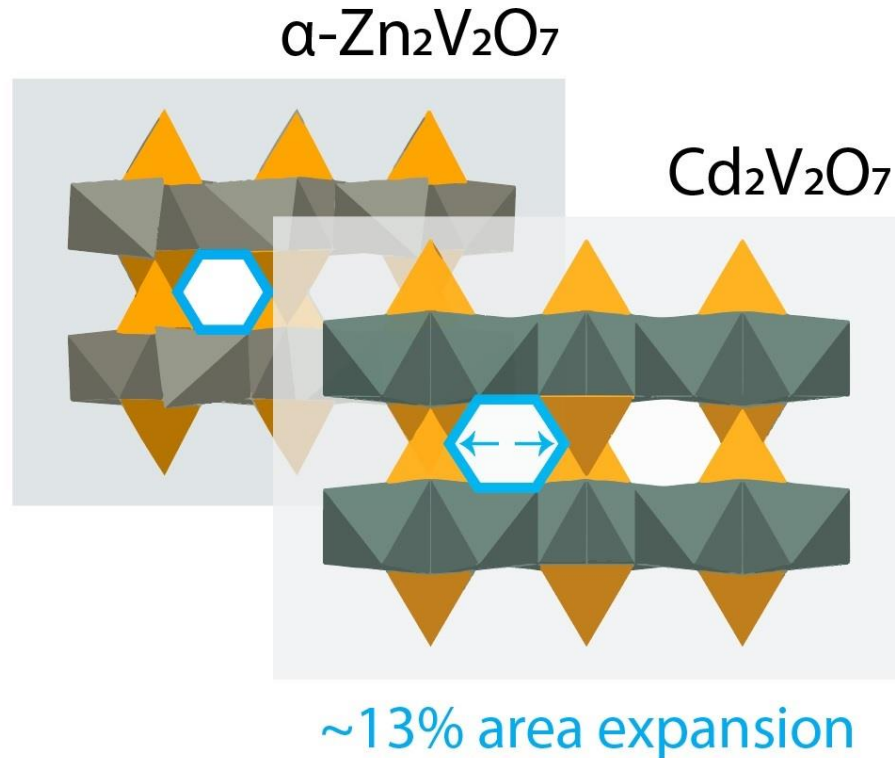
Vertical list of elements on the right:

- 12 IIB 2B
- 30 Zn Zinc 65.39
- 48 Cd Cadmium 112.411
- 80 Hg Mercury 200.59
- 112 Cn Copernicium [277]

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 pentoxide (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 pentoxide doped with Cd (1%, 5%, and 10%)

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

C. Cd vanadates (CdV_2O_6 and $Cd_2V_2O_7$)

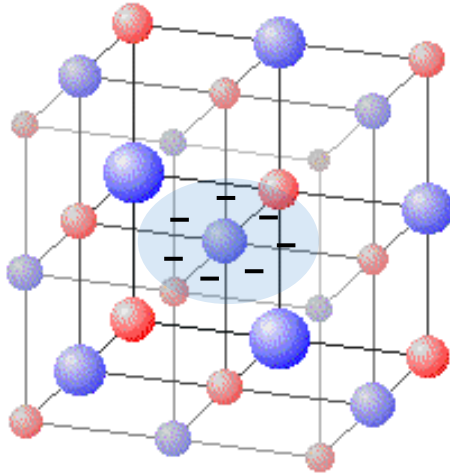
- i) Sol-gel prepared from pure elements V and Cd

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)

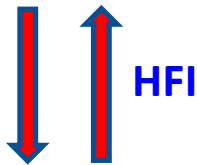
Electric Interaction



Electron charge density



Electric field Gradient (V_{ij})



Nuclear quadrupole moment

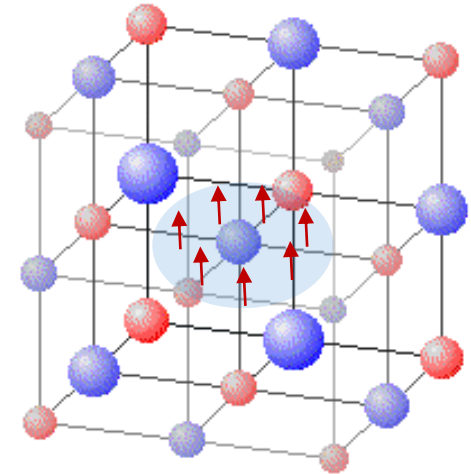


Probe nucleus



Nuclear dipole magnetic moment

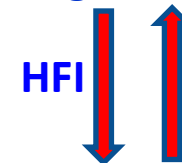
Magnetic Interaction



Electron spin density



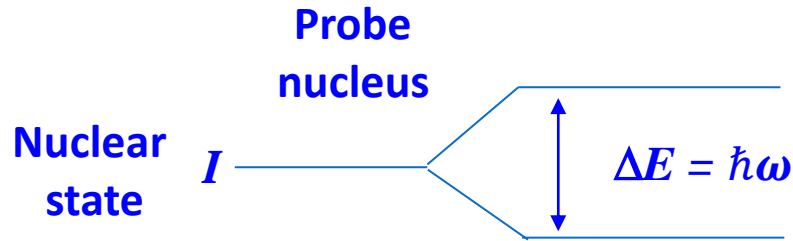
Magnetic field (B_{hf})



Perturbed angular correlation

Electric Interaction

Magnetic Interaction



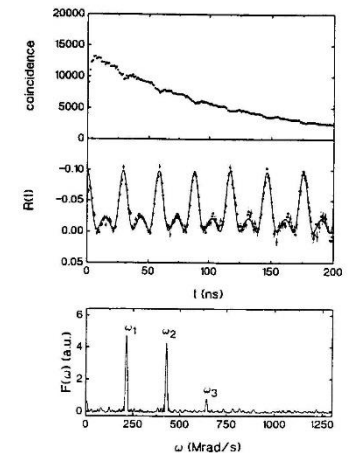
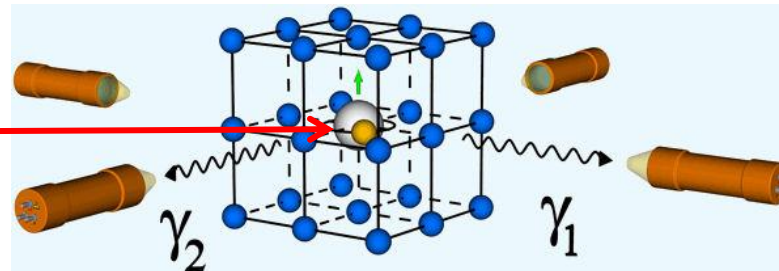
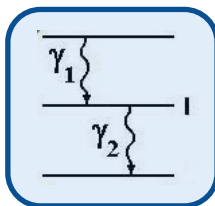
$$\omega_Q = \frac{eQV_{zz}}{4I(2I-1)\hbar}$$

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

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

Perturbed Angular Correlation (PAC)

Radioactive probe nucleus



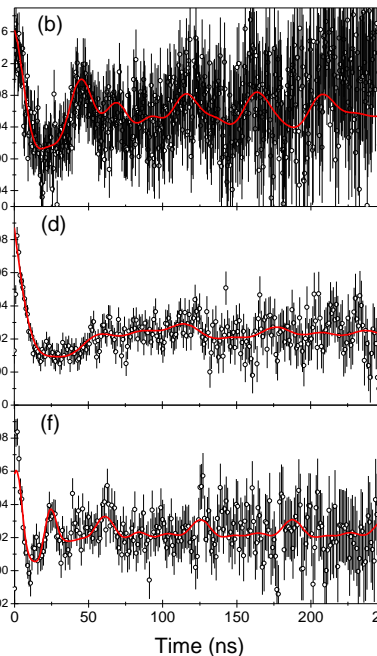
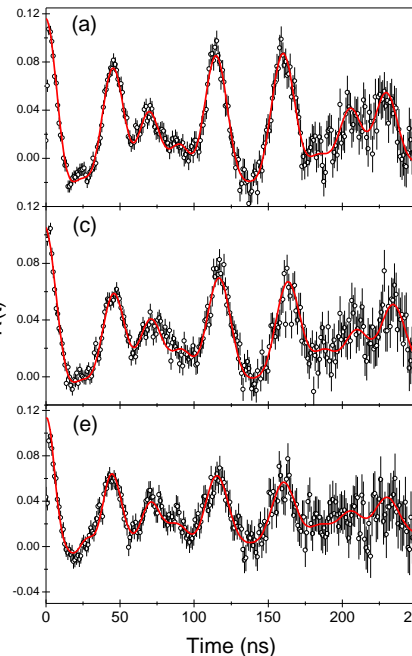
RESULTS

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.

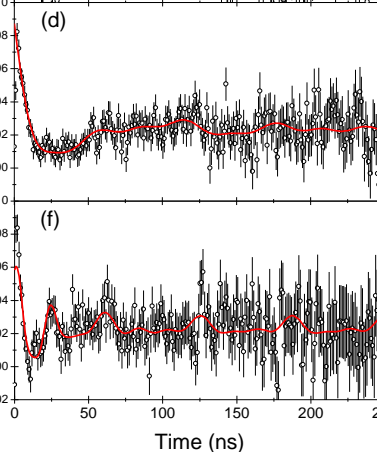
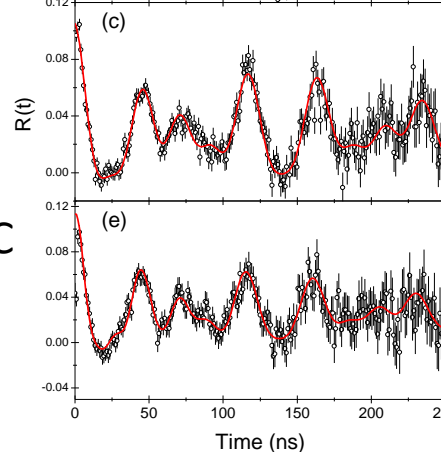
The best annealing was a mix of dynamic vacuum (**DV**) for 5 min, static vacuum (**SV**) for 5 min, followed by annealing in air for 5 min, hereafter called **555 annealing**.

COM-555 at 500 °C



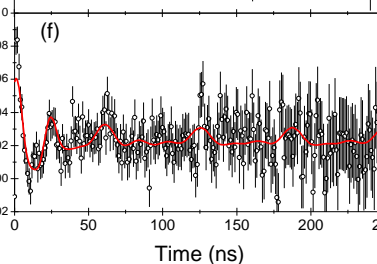
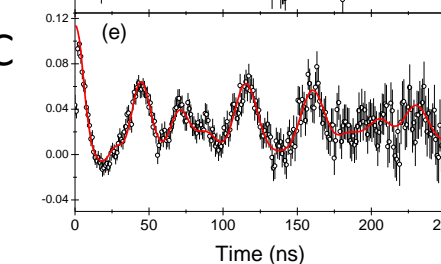
COM-AIR at 500 °C
for 20 min

SG-555 at 570 °C



SG-DV at 500 °C
for 20 min

COM-555 at 570 °C



SG-AIR at 500 °C
for 20 min

Results

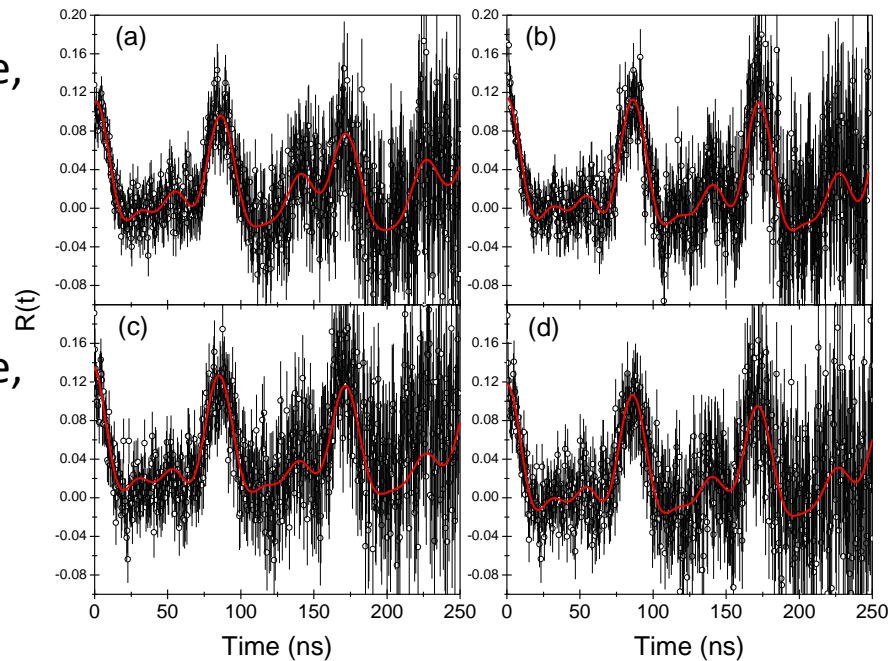
we tested the hypothesis of a thermal reduction of V_2O_5 to VO_2 (via annealing at 600 °C during evacuation)

COM sample,
under SV

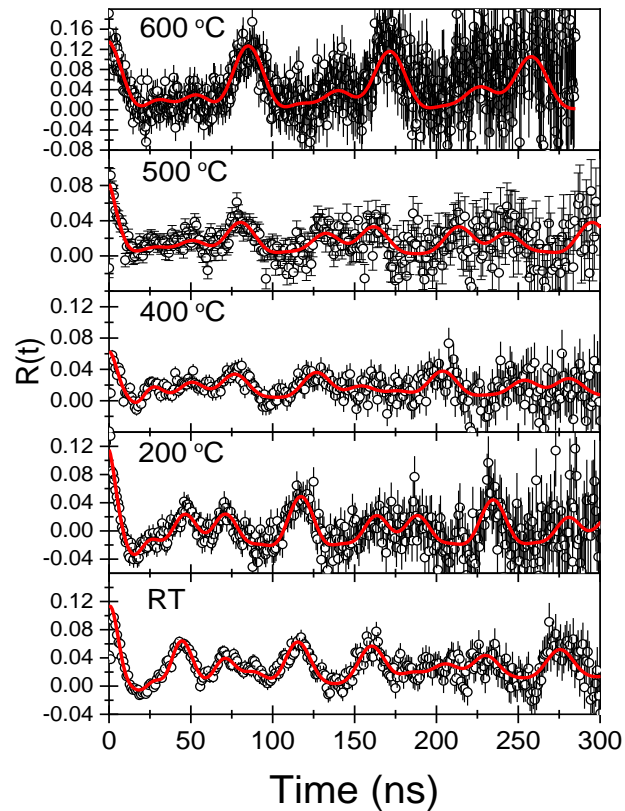
COM sample,
under DV

COM sample,
in AIR

SG sample, in
AIR

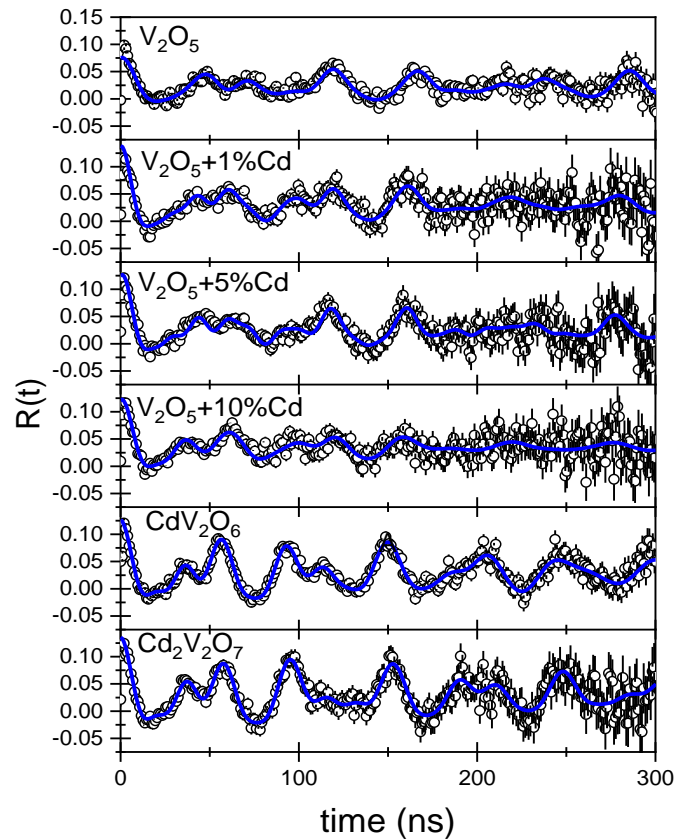


Results



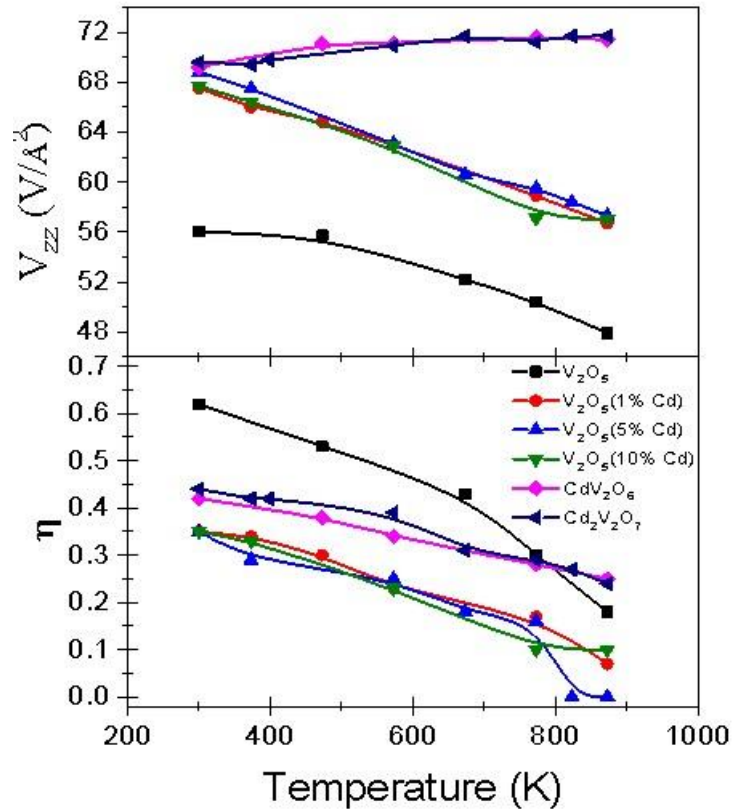
V_2O_5 COM samples measured at different temperatures in AIR

Results



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

Results and Discussion



Values of V_{zz} for Cd-doped V_2O_5 and for V_2O_5 decrease when temperature increases.

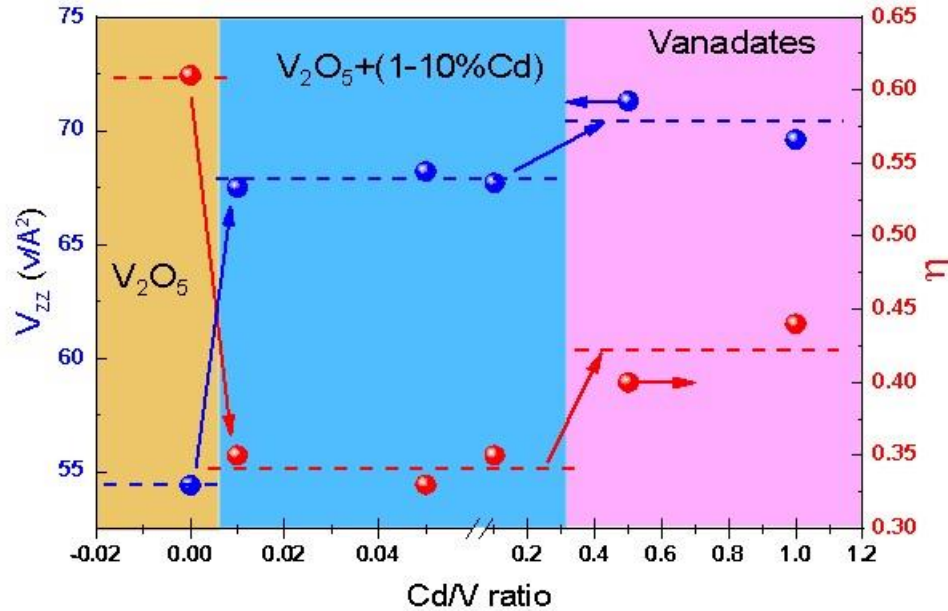
V_{zz} for vanadates is almost independent of temperature

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 an 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 V_{zz} 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 $^{111\text{m}}\text{Cd}$ 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