Comments on

IRIS Assessment Plan for Inhalation Exposure to Vanadium and Compounds (Scoping and Problem Formulation Materials)

Sarbajit Banerjee, *Ph.D., FRSC, FInstP*

Davidson Chair in Science | *Professor of Chemistry* | *Professor of Materials Science & Engineering* | *Chancellor EDGES Fellow*

Texas A&M University

Sarbajit Banerjee, PhD, FRSC, FInstP

- I lead a research group (3 post-doctoral researchers, 17 PhD students) focused on the design and creation of vanadium compounds for applications in clean energy, energy-efficient electronics, and sustainable infrastructure. Our particular interest is in the structural chemistry and reactivity of vanadium oxides.

- I have authored 200+ peer-reviewed scientific articles that have been cited in excess of 12,000 times with an h-index of 55

- Research accomplishments recognized by: National Science Foundation CAREER award (2009); the American Chemical Society ExxonMobil Solid-State-Chemistry Faculty Fellowship (2010); the Cottrell Scholar Award from the Research Corporation for Science Advancement (2011); the Minerals, Metals, and Materials Society Young Leader Professional Development Award (2013); Journal of Physical Chemistry Lectureship (2013); MIT Technology Review “Top 35 innovators under the age of 35” (2012); Institute of Materials, Minerals, and Mining (IOM3) Rosenhain Medal and Prize (2015); IOM3, Royal Society of Chemistry, and the Society for Chemistry & Industry Beilby Medal and Prize (2016); NASA NIAC Fellow (2021); NSF Special Creativity Extension Award (2020, 2021)

- My comments today are my own and do not represent those of any other organization or company

Overview of Comments

- ❑ Comments on motivation of study
- ❑ Study quality and specifications related to speciation of vanadium compounds
- ❑ Comments on science topics

Comments on Motivation for Study

"Results for a commercially available V-SCR reveal that both V and W release begin at 500°C"
Significantly above temperatures for Nonroad Transient Cycle (NRTC) and 8-mode Nonroad Steady Cycle (NRSC) tests.
"The maximum V-SCR temperature during the NRTC is less than 360°C while the V-SCR reaches a temperature of 481°C during the hotter NRSC. In this case, SCR temperatures during nonroad certification cycles, representative of typical operation, are maintained below the 500°C release threshold."

Hohl *et al*. have examined vanadium catalysts embedded in monoliths and find that vanadium compound sublimation is observed only above 700°C

- A catalytic convertor after 200, 000 miles of use does not show a significant reduction in catalytic activity or statistically differentiable loss in mass that would point to vanadium release (Liu *et al*) .

Schobing *et al*. report in a recent comprehensive study of commercial full-body-type vanadia-based SCR catalyst with a density of 300 cpsi published in 2018: *"no significant vanadium sublimation occurred at temperatures less than 675 °C. Moreover, it was observed that the DeNOx activity of the monolith sample remains stable at 550 °C during 10 h of exposure*

Liu, Z. G.; Ottinger, N. A.; Cremeens, C. M. Vanadium and tungsten release from V-based selective catalytic reduction diesel aftertreatment. *Atmospheric Environment* **2015**, *104*, 154-161.
Hohl, Y.; Vonarb, R.; Moreau, P.; Valero, P.; Tschamber, V.; Brillard, A.; Brilhac, J.-F.: Investigation of vanadium sublimation from SCR catalysts. SAE International, 2015, DOI: 10.4271/2015-24-2503
Schobing, J.; Tschamber, V.; Brilhac, J.-F.; Auclaire, A.; Hohl, Y. Simultaneous soot combustion and NOx reduction over a vanadia-based selective catalytic reduction catalyst. Comptes Rendus Chimie 2018, 21, 221-231.

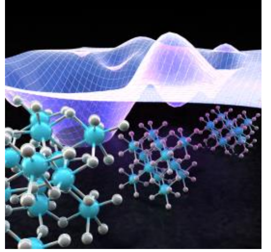
Limitations of Studies Examining Inhalation Exposure of Vanadium Compounds

- Studies considered are substantially deficient as compared to studies designed for testing of toxicity of small molecules and product safety evaluation
- Test compound often not sourced or analyzed with respect to critical parameters controlling environmental fate, transport, and toxicity
- Speciation of vanadium almost entirely neglected
- Quantitative measures of vanadium exposure are highly variable and often lacking in rigor

Unlike small molecules, the potential ecological toxicity and health risks of periodic solids needs to be evaluated as a function of crystal structure as well as with reference to factors such as crystallite size, particle size, crystallinity, surface planes exposed, presence of impurities, surface passivation, and speciation under ambient conditions. The fundamental physical properties and reactivities of the vanadium compounds under consideration depend strongly on all of these parameters

Chen, M.; Zhou, S.; Zhu, Y.; Sun, Y.; Zeng, G.; Yang, C.; Xu, P.; Yan, M.; Liu, Z.; Zhang, W. Toxicity of carbon nanomaterials to plants, animals and microbes: Recent progress from 2015-present. *Chemosphere* **2018**, *206*, 255-264.
Uo, M.; Akasaka, T.; Watari, F.; Sato, Y.; Tohji, K. Toxicity evaluations of various carbon nanomaterials. *Dental Materials Journal* **2011**, 1105140126-1105140126.
Shoults-Wilson, W. A.; Reinsch, B. C.; Tsyusko, O. V.; Bertsch, P. M.; Lowry, G. V.; Unrine, J. M. Role of Particle Size and Soil Type in Toxicity of Silver Nanoparticles to Earthworms. *Soil Science Society of America Journal* **2011**, *75*, 365-377.
Park, M. V. D. Z.; Neigh, A. M.; Vermeulen, J. P.; de la Fonteyne, L. J. J.; Verharen, H. W.; Briedé, J. J.; van Loveren, H.; de Jong, W. H. The effect of particle size on the cytotoxicity, inflammation, developmental toxicity and genotoxicity of silver nanoparticles. *Biomaterials* **2011**, *32*, 9810-9817
Warheit, D. B.; Webb, T. R.; Colvin, V. L.; Reed, K. L.; Sayes, C. M. Pulmonary Bioassay Studies with Nanoscale and Fine-Quartz Particles in Rats: Toxicity is Not Dependent upon Particle Size but on Surface Characteristics. *Toxicological Sciences* **2006**, *95*, 270-280.

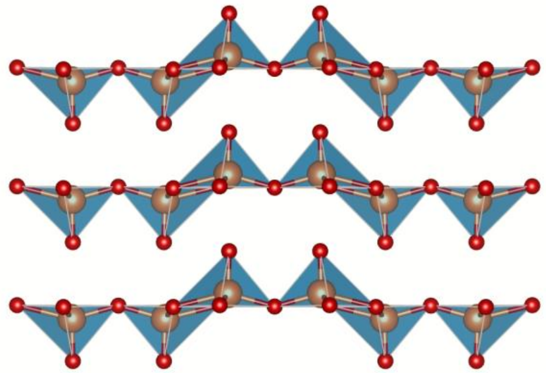
Composition alone is not enough



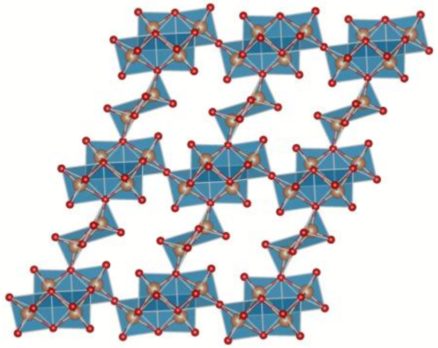
Vanadium oxides have rugged energy landscapes characterized by a plethora of structures

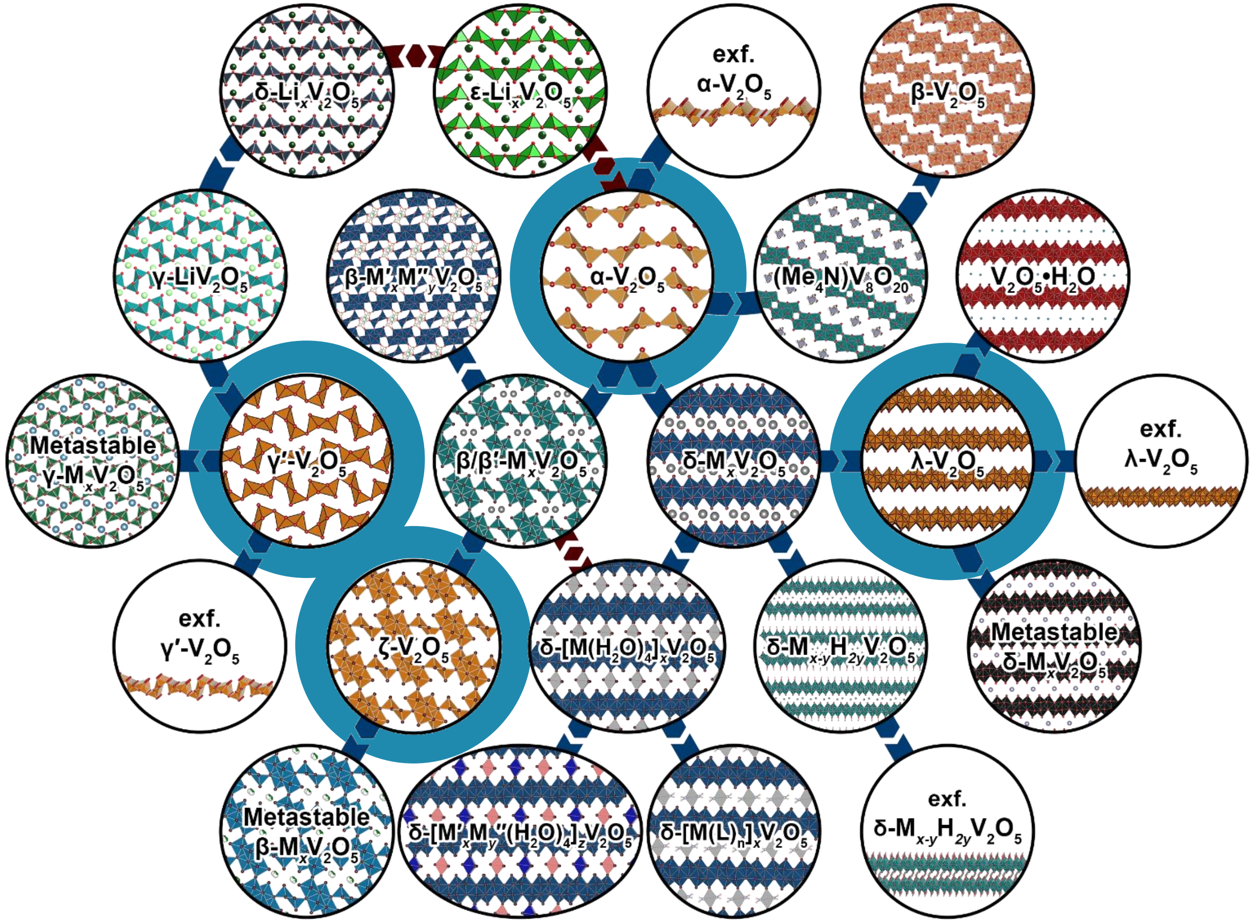
Polymorphism in V_2O_5

α-V_2O_5

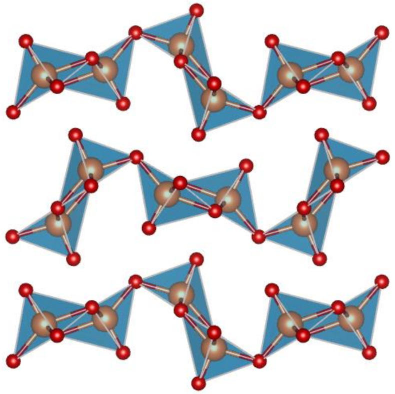


ζ-V_2O_5

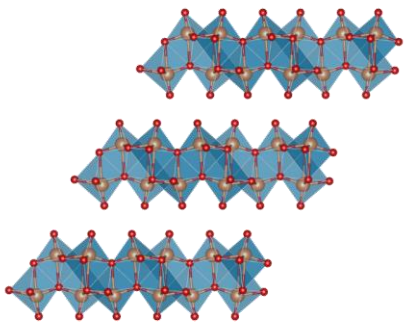




γ′-V_2O_5



λ-V_2O_5

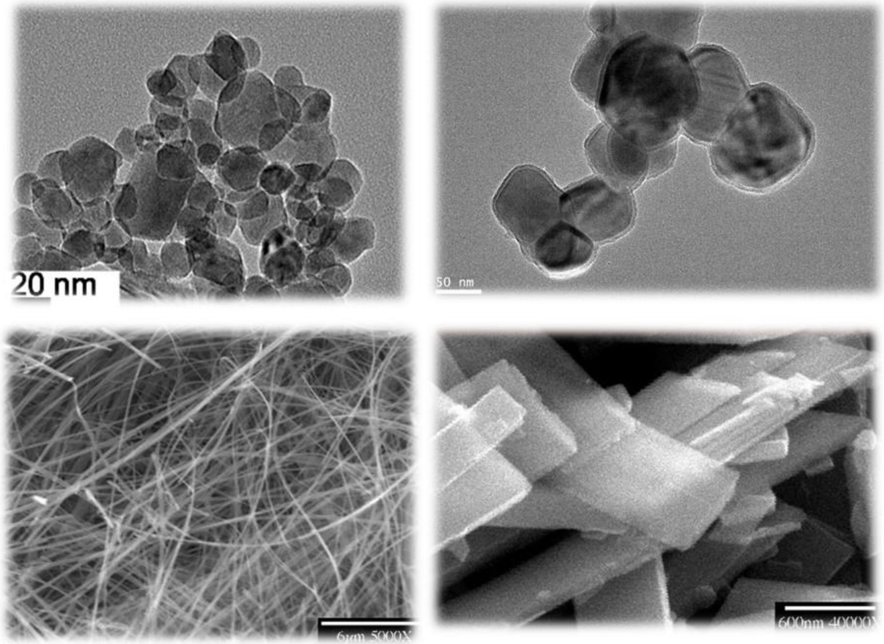


Parija, Waetzig, Andrews, Banerjee. *J. Phys. Chem. C.* ***2018***, 122, 25709.
De Jesus, L. R.; Andrews, J. L.; Parija, A.; Banerjee, S. Defining Diffusion Pathways in Intercalation Cathode Materials: Some Lessons from V2O5 on Directing Cation Traffic. ACS Energy Letters 2018, 915-931.
Andrews, J. L.; Santos, D. A.; Meyyappan, M.; Williams, R. S.; Banerjee, S. Building Brain-Inspired Logic Circuits from Dynamically Switchable Transition-Metal Oxides. Trends in Chemistry 2019, 1, 711-726.
Parija, Liang, Andrews, De Jesus, Prendergast, Banerjee. *Chemistry of Materials*, **2016,** *28*, 5611.

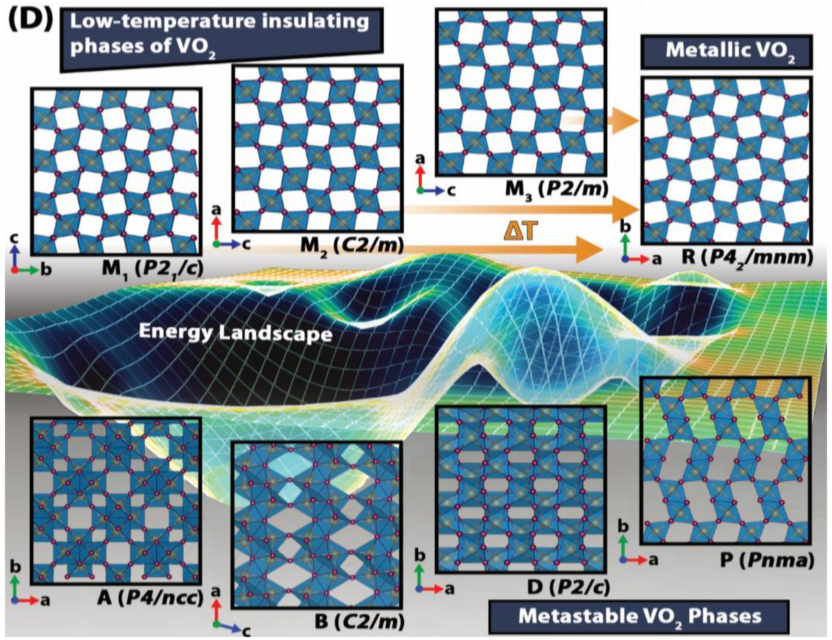
Key Science Issues: PECO Criteria

For animal studies, the following information was captured: chemical form

For human studies, the following information was summarized: chemical form; population type



limiting speciation studies of vanadium to chemical composition and oxidation state is an oversimplification that ignores the fundamental tenets of chemical reactivity and biological activity of solids



Parija, Waetzig, Andrews, Banerjee. Traversing Energy Landscapes Away from Equilibrium: Strategies for Accessing and Utilizing Metastable Phase Space *J. Phys. Chem. C.* ***2018***, 122, 25709.
De Jesus, L. R.; Andrews, J. L.; Parija, A.; Banerjee, S. Defining Diffusion Pathways in Intercalation Cathode Materials: Some Lessons from V_2O_5 on Directing Cation Traffic. ACS Energy Letters 2018, 915-931.
Andrews, J. L.; Santos, D. A.; Meyyappan, M.; Williams, R. S.; Banerjee, S. Building Brain-Inspired Logic Circuits from Dynamically Switchable Transition-Metal Oxides. Trends in Chemistry 2019, 1, 711-726.
Justin L Andrews, Peter Stein, David A Santos, Cody J Chalker, Luis R De Jesus, Rachel D Davidson, Michelle A Gross, Matt Pharr, James D Batteas, Bai-Xiang Xu, Sarbajit Banerjee, Curvature-Induced Modification of Mechano-Electrochemical Coupling and Nucleation Kinetics in a Cathode Material. Matter 2020, 3, 1754-1773. DOI: 10.1016/j.matt.2020.08.030