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Oxovanadium electronics for in-memory, neuromorphic, and quantum computing applications

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Vanadium is a critical raw material. In the nearby future, it may, however, become one of the key elements of computer devices based on two-dimensional arrays of spin qubits for quantum information processing or charge- and resistance-based data memory cells for non-volatile in-memory and neuromorphic computing. The research and development (R&D) of vanadium-containing electronic materials and methods for their responsible fabrication underpins the transition to innovative hybrid semiconductors for energy- and resource-efficient memory and information processing technologies. The combination of standard and emerging solid-state semiconductors with stimuli-responsive oxo complexes of vanadium(*v,v*) is envisioned to result in electronics with a new room-temperature device nanophysics, and the ability to modulate and control it at the sub-nanometer level. The development of exponential (Boolean) logics based on the oxovanadium-comprising circuitry and crossbar arrays of individual memristive cells for in-memory computing, the implementation of basic synaptic functions via dynamic electrical pulses for neuromorphic computing, and the readout and control of spin networks and interfaces for quantum computing are strategically important future areas of molecular chemistry and applied physics of vanadium.

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Need for transformation of current silicon technology

The disruptive transformation of the landscape of modern computer technologies to produce semiconductor microcircuits into energy- and resource-efficient micro- and nanoelectronics with increased functionality (in particular, “More than Moore” devices) requires innovations and bundled efforts at different levels of fundamental research and technology development. This R&D is especially needed due to the growing influence of high power-consuming artificial intelligence (AI) algorithms¹ (like *e.g.* ChatGPT) and the overall negative impact of information and communications technologies (ICT) on the environment and economy.^{2,3} Research into the spin properties of molecular qubits and charge properties of molecular multi-logic networks, that provide digital (discrete) or analog (continuous) switching functions at room temperature and low potentials on complementary metal oxide semiconductor (CMOS) surfaces as well as surfaces extended by functional two-dimensional (2D) materials,⁴ is a promising path not only to greener computing, but also to technologies with more natural interfaces. The academic silicon technology roadmap offered by the Japan Society of Applied Physics (JSAP) suggests

that the integration of CMOS technology with 1-nm molecular technology might be achieved by 2045.

Responsible electronics, miniaturisation, and natural interfaces (see Si technology roadmap of JSAP), that open access to new added functionality and efficiency of future computer chips, are the main drivers of the Si-based computing technology transformation. The search for innovative materials as active electronic (memristive⁵) layers on a single chip, inspired in many ways by brain biology (Table 1), is at the heart of highly sought-after transition to green IT.

From a chemical perspective, breakthroughs in the eco-friendlier preparation of new functional electron transport and switching compounds and related bioinspired/biomimetic materials can be achieved through automation in the chemistry lab.⁶ The latter allows among other things for controlled, computer-assisted reactions in continuous flow supported by in-line/online acquisition of data. However, this automation also requires significant improvements in the data- and energy-efficient machine learning models. From an engineering perspective, it is necessary to develop methods for non-destructive, spatially controlled processing of new, synthesised, low-dimensional compounds from a solution or from the gas phase onto scalable device architectures. For example, mass-selective ion soft-landing⁷ and ink-jet printing⁸ techniques offer significant opportunities for creating switchable molecularly functionalised surfaces outside of cleanroom conditions.

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Table 1 CMOS technology vs. brain biology. A comparison of computer and bioelectronic attributes

| | Insulating material | Voltage-gated channels to control electrical current | Memory storage units | Arithmetic and logic operations |
|--------------------|---------------------|--|---|---------------------------------|
| Technical systems | SiO ₂ | Thin-film field-effect transistor | Logic gate (<i>e.g.</i> , memristor) on a crossbar array | Arithmetic logic unit |
| Biological systems | DNA | Cell membrane ion channel | Synapse in a neural network | Neuron |

A look at the landscape of various semiconductor materials currently being developed for CMOS and beyond-CMOS technologies shows that compounds containing vanadium atoms as redox- and spin-active centres have the potential to become important components of next-generation computing devices.

Vanadium as a potential game changer

The unique combination and responsive character of physical state variables (charge, spin, and phase) of vanadium,⁹ a transition metal [Ar]3d³4s² from group 5 of the periodic table, grants access to advanced electrical, magnetic, optical, thermo-chromic, and electrochemical properties of its highest valent (V⁵⁺) and lower valent (V⁴⁺, V³⁺, and V²⁺) compounds.^{10–12} Also, the electronic properties of materials from other chemical classes benefit from the inclusion of vanadium, such as *e.g.* silicon carbide, where the spin- $\frac{1}{2}$ V⁴⁺ ions can be implanted as quantum emitters.¹³ Cesium vanadium antimonide¹⁴ (CsV₃Sb₅) exhibits unconventional physics¹⁵ including bulk superconductivity in single crystals due to a two-dimensional (2D) Kagome network of mixed-valent vanadium ions. These properties are of great importance for the emerging era of AI systems, quantum computation and communication, as well as for the electrification of the automotive industry.

Vanadium supply

Vanadium belongs to the fifth list 2023 of critical raw materials for the European Union (EU).¹⁶ Its world's largest producers are China (>60%), Russia, and South Africa, which account for approx. 75% of global vanadium supply.¹⁷ In view of the growing demand¹⁸ for this metal and its compounds, it is important that the European industrial sector considers its “vanadium sovereignty”. One of the strategic projects for domestic supply is the Vanadium Recovery Project in Finland.¹⁷

In addition to the current extensive industrial research on vanadium as a battery material,¹⁹ growing attention to vanadium is attached to its oxide and oxo compounds for digital and analog computing. According to the ‘Supply chain analysis and material demand forecast in strategic technologies and sectors in the EU – A foresight study’ by the European Commission,²⁰ vanadium(v) pentoxide V₂O₅ as a processed material can be used in the data transmission networks, where printed circuit boards, optoelectronic components, semiconductors, and sensor chips play a significant role. The production of V₂O₅ from the vanadinite mineral²¹ Pb₅(VO₄)₃Cl with naturally occurring deposits, *e.g.*, in Spain or Scotland might provide an interesting source of vanadium for innovative vanadium-based nanomaterials for the EU. It

is noteworthy that V₂O₅ is often a precursor in the wet-chemical synthesis of starting reagents for soluble molecular vanadium oxides, so-called polyoxovanadates. The latter also occur in natural mineral phases.²² Another type of oxovanadium compounds that may have potential applications in some form in computing are vanadyl porphyrins.²³ These vanadium(IV) complexes (see, a crystal structure of a synthetic vanadyl petroporphyrin²⁴) were detected *e.g.* in Venezuela Orinoco heavy crude oil by using Fourier transform-ion cyclotron resonance mass spectrometry²⁵ or could be extracted from oil of the North Buzachi oil-and-gas-bearing region in Kazakhstan.²⁶ Overall, fully-oxidised, mixed-valent, and fully-reduced polyoxovanadates^{27–29} and macrocyclic vanadyl compounds^{30–32} are currently being actively studied in the fields of data storage, data processing, and biomedical technologies.³³

Oxides and oxo complexes of vanadium

In the area of oxide-based memory materials, vanadium dioxide³⁴ VO₂ and trivanadium pentoxide³⁵ V₃O₅ thin films have been found to show thermally induced insulator-to-metal transition behaviour. This property and the emerging physics have great implication for neuromorphic computing³⁶ with vanadium-based memristors as artificial synapses.

Integrating molecular compounds with discrete energy levels into *e.g.* memristive in-memory computing approaches^{37,38} should provide higher levels of precision and spatial control over the transfer of charge and spin through the switching material. This can be expected based on the diverse effects of tailored molecular functionalisation on the physical properties of *e.g.* two-dimensional (2D) material surfaces.^{39–44} Transferring the underlying principles of redox-based memristive switching of metal-oxide devices⁴⁵ to the level of interaction of molecular compounds, containing redox/spin switchable and/or photo inducible metal centres, with bound resistive oxide layers might become a useful lever for modulating electron transport and even for programming memristive characteristics of such electronic and spintronic heterostructures.

Molecular congeners of vanadium oxides⁴⁶ are mono- and polynuclear oxovanadium complexes. The latter can be divided into two qualified classes with the far-reaching potential for hybrid green IT technologies. Class I is represented by the neutral vanadyl complexes with *e.g.* dipivaloylmethane,⁴⁷ phthalocyanine⁴⁸ (Pc) or tetraphenylporphyrinate ligands.⁴⁹ Fig. 1a illustrates one of these compounds, namely VOPc that is synthesised⁵⁰ from phthalonitrile and VCl₃. The remarkable electronic and magnetic behaviour of I is due to the critical role of the vanadyl group⁵¹ VO²⁺ in a square-pyramidal coordination environment. These complexes exhibit the potential in the form

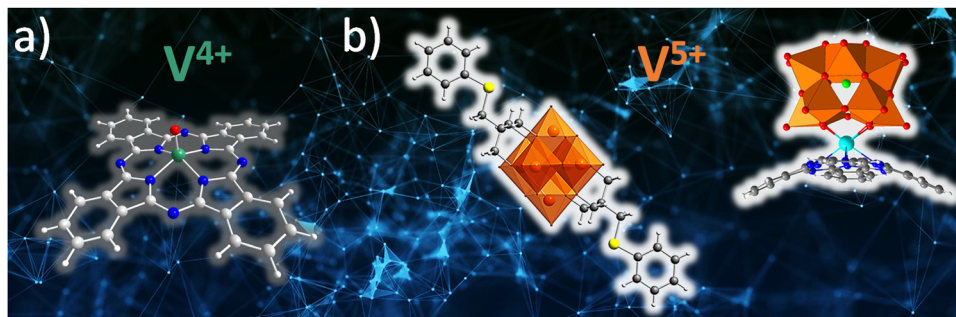


Fig. 1 Selected examples of micro-spectroscopically investigated spin- and redox-active oxovanadium structures. The structures are supported by organic ligands providing a stable interface with the substrate surface and determined by single-crystal X-ray diffraction: (a) sublimable VOPc compound with a V^{4+} centre and (b) solution-processable $[V_6O_{13}((OCH_2)_3C-R)_2]^{2-}$ (R is an organic or organometallic moiety) and $[HV_{12}O_{32}Cl(LnPc)]^{3-}$ (Ln is a lanthanide; Pc is phthalocyanine) with V^{5+} centres. Counter cations of the anionic compounds are not shown. Colour code: V^{4+} = green, V^{5+} = orange, O = red, S = yellow, Cl = pale green, N = blue, C = grey, Ln = turquoise.

of processable molecular spin qubits with long coherence times for quantum memories.

The vanadyl VO^{2+} can be found in the mineral cavansite $Ca(VO)Si_4O_{10} \cdot 4H_2O$, but also in synthetic semimetal-functionalised polyoxovanadates²⁷ such as *e.g.* the $[V_{12}As_8O_{40}(HCO_2)]^{5-}$ anion⁵² with $V^{4+}_8V^{5+}_4$ centres from class II. This spherically shaped, arsenato-substituted polyoxovanadate has been regarded as a quantum cellular automata.^{53,54}

In addition to fully-reduced and mixed-valent derivatives, class II contains fully-oxidised polyoxovanadate anions, charged balanced *e.g.* by quaternary alkyl ammonium or alkali metal cations. Their high-performance representatives (Fig. 1b and c), the bis(trisalkoxo)-ligated Lindqvist-type hexavanadates⁵⁵ with octahedrally coordinated vanadium(v) centres and the tubular dodecavanadate cages composed of square-pyramidal VO_5^{5-} groups (one lacunary position is covalently blocked by a lanthanide (Ln) phthalocyanine moiety⁵⁶) have emerged to be promising polyoxometalate (POM) candidates for molecular charge- and resistance-based memories.^{57,58} These ion species show unprecedented physical multi-state switching at the level of single molecules^{59,60} as well as thin films⁶¹ in response to an external potential-induced electrical field of a scanning tunneling microscope (STM) tip. As soluble compounds, these polyoxovanadates can be processed from solution to the gas phase⁶² and onto surfaces. Thus, their synthesis could be scaled up by automating reactions in a continuous flow that follows a low thermal budget approach in the preparation of switching materials with improved chemical and waste management. Materials reinforced with such POM structures promise to open up a revolutionary way to store digital information in wafer-scale hybrid devices, including neuromorphic devices based on ink-jet printed filaments.⁶³

The molecular candidates from classes I and II also provide great opportunities for the realisation of brain-inspired molecularly empowered classic and quantum logic gates for information processing,⁶⁴ *e.g.* by the on-surface implementation of low-/high-potential counterpart switches with substantially different band gaps, spin qubit arrays, and/or by tuning the molecular conductance through counter cations in the case of polyoxoanionic ground-state structures. Their integration as

spin qubits, electrical or opto-electrical switches, and/or conductance modulating agents at the level of single molecules or nano-machined thin films onto CMOS compatible material systems clearly paves the way for wafer-scale bottom-up neuromorphic electronics and spintronics. This rapidly developing field of materials can be seen as part of molecular cybernetics, *i.e.* the integration of molecular charge- and spin-based electronics and computational cybernetics. However, the technologically crucial transition from fundamental classical or spin-polarised STM-based model studies to real-world electrical contacting of I and II remains the biggest challenge of research and development at the interface of molecular inorganic chemistry, condensed matter solid physics, and device engineering.

Polyoxovanadates: from single molecules to layers – what's next?

Recently, a technologically important departure from experiments with single molecules⁶⁵ to the solution-processed formation and multi-state switching of monolayers of polyoxovanadates⁶¹ has been realised. The latter can be modified into structured patterns by using STM nanomachining. However, there remain a number of important unresolved issues at the level of single molecules and thin films, in particular multi-state on/off reversibility and hysteresis behaviour of polyoxovanadate compounds, that need to be addressed in further research.

The combination of polyoxovanadates with the family of existing, technically suitable switching materials (*e.g.*, metal oxides,⁶⁶ metal alloys as phase change materials,⁶⁷ 2D transition metal chalcogenides,⁶⁸ and MXenes⁶⁹), that are currently being exploited or developed for digital and analog computing, represents another challenging task. The combination of both classes I and II together in one hybrid switching material system might offer an interesting approach to exponential logics. Moreover, due to their rich molecular magnetism, the possibilities of chemical design⁷⁰ of reduced and mixed-valent polyoxovanadates as potential spin qubits merit further investigation in the field of spintronics and quantum information.

The role of counteractions⁷¹ in the electron transport and switching properties of devices with embedded POM functionalities is not yet fully understood, so that further mechanistic studies are needed.

Concluding remarks

Key points:

- Vanadium is a critical raw material.
- Vanadium oxides have characteristics important for quantum and memristive materials.
- VO₂ thin films exhibit thermally induced insulator-to-metal transition.
- V₂O₅ is often used in the synthesis of molecular oxovanadium(IV,V) complexes.
- Vanadyl fragment is an important object of research in quantum information processing.
- Polyoxyvanadates behave as electrically accessible multi-state switches at room temperature, currently exhibiting retention times ranging from a few ms to approximately 300 ms.
- Electrical contacting and integration of oxovanadium(IV,V) thin films at the wafer scale is one of the biggest challenges towards functional molecular electronics and molecular memristive computing.

Further research and development should be aimed at (i) the computer-assisted, controlled wet-chemical synthesis, (ii) surface engineering of large-area ‘oxovanadium switch–electrode surface’ interactions, (iii) solution-processed molecular printing of macro-/micro-/nano-objects, and (iv) their electrical measurements by a macroscopic external voltage source. In this endeavor, one important challenge is the tailoring of oxovanadium(IV,V) compound ligands to achieve chemically and thermally stable, surface-selective structures and their stimuli-responsive arrays, as well as to enhance interface effects on the physical properties of the switching materials in contact with technical electrode contacts. These studies will ultimately pave the way for the determination of important device parameters with integrated oxovanadium electronics such as endurance, retention times, uniformity, statistical variability, and electrical and mechanical reliability.

Conflicts of interest

There are no conflicts to declare.

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