

## MAGNETO-IONICS

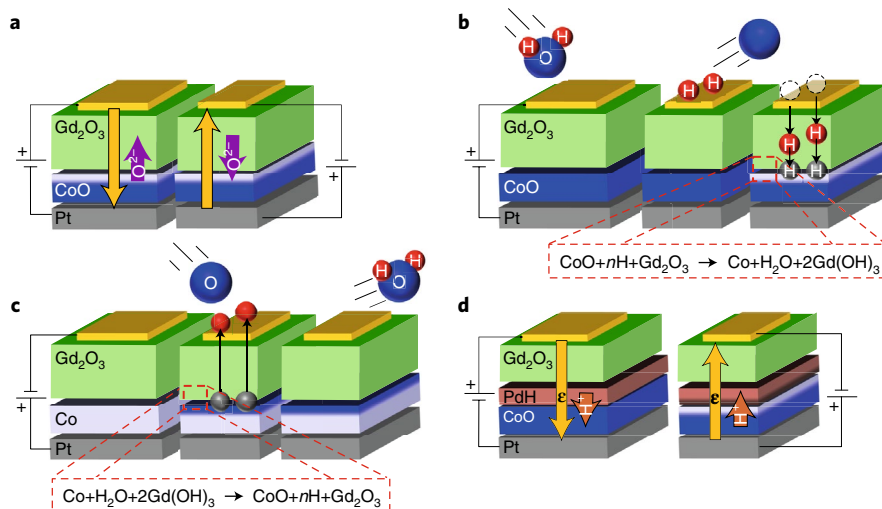
# Hydrogen finds a home in ionic devices

Hydrogen from surface-based electrolysis is implicated in the operation of high-speed magneto-ionic devices. Functionalizing this discovery, a new family of potentially high-speed, high-efficiency ionic devices is born.

Dustin A. Gilbert and Alexander J. Grutter

Picture the differences between silver, a shiny conductive metal, and silver tarnish, its matte insulating oxide counterpart. At the atomic level, the difference between these materials is merely the presence of a few oxygen ions; so that by reorganizing the ions in tarnish using, for example, an electric field, we may be able to locally recover some of the metallic silver and its functional properties. Indeed, this was the premise ten years ago when ionic control of resistance was first popularized through the memristor<sup>1</sup>. However, virtually every property of a material changes upon oxidation, and thus the same approach may enable control of magnetic, optical, thermal and mechanical properties as well<sup>2</sup>. In 2014, electric field-induced oxygen migration was presented as a method to control magnetism and magnetic anisotropy in a new field termed magneto-ionics<sup>3–5</sup>. These technologies married traditional electronics with spintronics (for example, magnetism-based memory and logic technologies). Now, writing in *Nature Materials*, Aik Jun Tan and colleagues<sup>6</sup> implicate a new mechanism for magnetization control that relies on hydrogen being forcefully extracted from moisture in the air as a crucial, and previously unknown, component in this process. Harnessing this discovery, the authors develop a new class of devices in which the magnetic properties are controllable by electric field-moderated hydrogen migration. The small size, low-atomic weight and weaker binding energy of hydrogen, as compared to oxygen, means that these devices might operate much faster than their oxide counterparts.

The authors first investigate two prototypical magneto-ionic devices, consisting of multilayer thin films of Pt/Co/Gd<sub>2</sub>O<sub>3</sub>/Au and Pt/CoO/Gd<sub>2</sub>O<sub>3</sub>/Au, under the premise that a voltage between the Au and Pt will drive oxygen ions into or out of the Co(O)/Pt interface and thus change the magnetic anisotropy (Fig. 1a). The authors initially investigate the role of the atmosphere surrounding the experimental device — surely, if ions are simply moving between the Gd<sub>2</sub>O<sub>3</sub> and the Co(O), one would not expect the atmosphere to affect



**Fig. 1 | Operation of magneto-ionic thin-film stacks.** **a**, A traditional magneto-ionic device, predicated on electric field-induced oxygen migration. **b**, A magneto-ionic device predicated on extracting hydrogen from the surrounding atmosphere, which is then used to reduce CoO. **c**, The reverse operation of **b**. **d**, A new magneto-ionic device architecture utilizing a built-in PdH reservoir as the hydrogen source. The solid yellow arrow represents the direction of the electric field.

the performance. Surprisingly, the authors show that these devices do not function in vacuum or dry nitrogen while in an atmosphere of dry oxygen the devices function very slowly. In contrast, in ambient air or ‘wet’ nitrogen — achieved by bubbling nitrogen through water — the devices work at high speeds. Recognizing that the device operates only at voltages greater than 1.5 V, closely matching the standard breakdown potential of water, the authors propose that electrolysis is occurring at the Au surface, with the liberated hydrogen ions being pumped through the film (Fig. 1b). The injected hydrogen can either bind directly with the CoO or react with the oxide to form hydroxides or interstitial water. Applying the reverse voltage, interstitial water and hydroxides in the Gd<sub>2</sub>O<sub>3</sub> release oxygen, which reacts with the Co, and hydrogen, which is ejected (Fig. 1c).

Based on these results, it is reasonable to suggest that a hydrogen-based magneto-ionic device may work faster and more reversibly than oxygen-based devices, but


there is an Achilles’ heel: magneto-ionic devices with this structure must have access to ambient humid air. The authors overcome this limitation by demonstrating a new device architecture predicated on electric field-driven ion migration from a built-in hydrogen reservoir in the form of a PdH layer (Fig. 1d). The authors then demonstrate survivability of the device through >2,000 cycles with only a slight decay in device functionality and magnetization switching at a relatively high speed of 100 ms<sup>−1</sup>.

It is worthwhile to speculate on the practicality of realizing functional, scalable devices. Three challenges come to mind, with the first being that the improved mobility of hydrogen is partly due to weaker bonding. It is well known that in PdH, for example, even moderate heating or exposure to vacuum can readily induce hydrogen ejection<sup>7</sup>. This weak bonding may also lead to limitations on the long-term stability of such devices — for example, the hydrogen will dissipate simply due

to entropy-driven diffusion over the ten-year benchmark timeframe for archival data storage. It will be crucial to identify materials for both the reservoir and the active layer, which are able to retain hydrogen over long time periods, even at elevated temperatures (most consumer devices are rated to operate at up to 70 °C, and sometimes much hotter). A second issue with this ionic technology is the read/write times. While Tan et al. demonstrate a record-breaking (for magneto-ionics) switching time, significant improvement is required to compete with modern hard drives or spin-transfer torque RAM (another spintronic random access memory device), with 10-ms and 10-ns latencies, respectively. Finally, the formation of PdH from Pd induces a large (3.5%) lattice expansion commensurate with a transformation to a brittle semiconductor; fracturing from this strain has been previously identified as a failure mechanism in PdH<sup>7</sup>. Materials for hydrogen storage

must be developed that are compatible with semiconductor films and are able to survive through the expected  $>10^{15}$  cycles in their lifetime.

With so much potential and many challenges still to be explored, there is plenty of work left to do. The opportunities presented by these technologies include high scalability, non-volatility and energy efficiency, going straight to the heart of today's most critical technological challenges. A spintronic memory cell based on magneto-ionics is likely to be smaller than traditional dynamic DRAM and static SRAM cells, but it is also conceivable that this technology will rival even hard drive storage densities of  $>1\text{ TB in}^{-2}$ , and potentially much more with 3D stacking. As with memristors, the two-terminal structure of these devices present alluring parallels to neurons and correspondingly neuromorphic computing<sup>8</sup>. While this piece has focused on applications in data storage and logic

technologies, applications for on-demand magnetism and optical switching may already be accessible. 

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## 2D MATERIALS

# Memristors with distorted structures

Structural transitions departing from the known phases of MoTe<sub>2</sub> are induced by applying a vertical electric field to multilayers of this material. These distorted structures show distinct conducting states that can be used for resistive memories.

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Materials that are known to exhibit multiple atomic structures or polymorphs are central to a spectrum of applications ranging from energy storage to information storage and electronic devices. For example, Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> alloys are commonly used in electronic devices to store a bit of information in the phase of the material, either amorphous or crystalline. While top-down engineering has pushed such devices all the way into commercial domains, a complete understanding at atomic scale of how the phases of these materials can be predictably engineered and switched is often lacking. This is particularly so for the case of resistive random access memory (RRAM) devices, where a sufficiently high field strength will induce an arrangement of defects or impurities that allow for the transport of charge through the material, thus allowing for control over the resistance state of the material to store information.

Writing in *Nature Materials*, Feng Zhang and colleagues<sup>1</sup> investigate a new twist on RRAM devices that could simplify and increase the ability to engineer such devices: the use of a layered material that is known to exhibit multiple similar energy crystal structures, MoTe<sub>2</sub>. The team reports that, unlike typical RRAM devices, MoTe<sub>2</sub> appears to form filaments that exhibit peculiar crystal structural characteristics, including a previously unidentified structure that the researchers refer to as 2H<sub>d</sub>. This structural state is different from the known 2H, 1T' or T<sub>d</sub> phases of this material and can be tuned to enter a high-resistance state (HRS) and low-resistance state (LRS) upon application of an electric field.

Layered transition metal dichalcogenides (TMDs) like MoTe<sub>2</sub>, exist in multiple crystal phases with differing electrical properties. For many TMDs, the 2H phase is semiconducting and has the lowest

energy among structural phases, while the 1T' phase is semi-metallic and metastable at room temperature. Among TMDs that follow this trend, MoTe<sub>2</sub> is known to have the smallest energy difference between the 2H and 1T' phases, making it a particularly good candidate for applications involving phase transitions between the 2H and 1T' phase<sup>2</sup>. Furthermore, the potential for monolayer MoTe<sub>2</sub> to be used in thermally driven<sup>3</sup> and electrostatically gated phase-change memory devices has been studied recently<sup>4</sup>, opening the possibility for MoTe<sub>2</sub> monolayers to be used in future electronic memory devices.

The experiments performed involve the creation of devices that are shown schematically in Fig. 1a. Here a voltage is applied to a pair of electrodes that sit above and below MoTe<sub>2</sub>. For sufficiently small voltages, MoTe<sub>2</sub> remains in the 2H phase, indicated by the low current values shown in red on the current–voltage (*I*–*V*) curve