Cationic Interstitials: An Overlooked Ionic Defect in Memristors

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Metal oxide-based memristors are promising candidates for breaking through the limitations in data storage density and transmission efficiency in traditional von Neumann systems, owing to their great potential in multi-state data storage and achievement of the in-memory neuromorphic computing paradigm. Currently, the resistive switching behavior of those is mainly ascribed to the formation and rupture of conductive filaments or paths formed by the migration of cations from electrodes or oxygen vacancies in oxides. However, due to the relatively low stability and endurance of the cations from electrodes, and the high mobility and weak immunity of oxygen vacancies, intermediate resistance states can be hardly retained for multilevel or synaptic resistive switching. Herein, we reviewed the memristors based on cationic interstitials which have been overlooked in achieving digital or analog resistive switching processes. Both theoretical calculations and experimental works have been surveyed, which may provide reference and inspiration for the rational design of multifunctional memristors, and will promote the increments in the memristor fabrications.

Keywords: resistive switching (RS), cationic interstitials, metal oxides, memristor, conductive filament

INTRODUCTION

As the memories and CPUs are separated in the current von Neumann computer system, the data have to be transferred between them through the limited bandwidth buses, which limits the time and energy efficiencies in the data processing. Such issue could be addressed by achieving an in-memory computing paradigm, for which the memristor is a suitable device because of its higher data storage density (Cheng et al., 2017; Chen et al., 2019) and excellent physical characteristics of conditional switching and physical MAC operation (Yang et al., 2017; Zhou et al., 2019; Xu et al., 2021; Li et al., 2022). Meanwhile, they can also bridge various electrical devices and be applied in energy storage, remote sensing, low-power applications, etc. (Chen, 2017; Han et al., 2020; Wang et al., 2020; Zhang and Sun, 2021) Thus, memristors are crucial for non-volatile memory, logic operations, Internet of Things, and neuromorphic computing in the big data era (Qin et al., 2020; Xu et al., 2020; Yao et al., 2020; Huang et al., 2021).

The memristor is a two-terminal electrical device that regulates the flow of electrical current in a circuit and remembers the amount of charge that has previously flowed through it even after removing the bias voltage (Fu et al., 2020). The original concept for memristors was proposed by Leon Chua in 1971, which was described as a nonlinear, passive two-terminal electrical component that linked electric charge and magnetic flux (Chua, 1971). This conceptual device has been firstly
linked to a kind of physical resistive switching device (ReRAM) by HP labs in 2008 (Strukov et al., 2008). Nowadays, the definition of memristor has been broaden to the arbitrary form of non-volatile memory with the foundation principle of resistance switching.

So far, the state transition phenomenon in different material systems is employed to trigger the resistive switching (RS) behavior and further construct the different types of memristors. Except for the well-studied RS behavior in metal-oxide materials (Illarionov et al., 2020; Liu et al., 2021; Wang et al., 2021), phase change materials (Hazra et al., 2021), organic materials (Chen, 2017; Cheng et al., 2017), ferroelectric materials (Guan et al., 2017), and magnetic materials (Park et al., 2018) are also reported to exhibit the macroscopic RS behavior because of the transition of crystalline phase, ferroelectric polarization, and spin polarization respectively. Among these numerous material systems, the metal-oxide-based memristors are promising owing to their low cost, simple process, and high compatibility with complementary metal-oxide-semiconductor (CMOS) technology (Mohammad et al., 2016; Illarionov et al., 2020; Nili et al., 2020).

However, compared to the basic metal-oxide-semiconductor (MOS) transistor which is the foundation device of constructing the current computing system, the memristor is still suffering from the relatively low reliability caused by device fluctuation, limited stability, and durability to maintain the resistance value or to improve repeated erasable times. Therefore, rational design and optimization of the memristor active layer through material engineering for enhancing the performance of memristors are expected. The works on metal-oxide-based RS have been mainly focused on the migration or ionization of oxygen vacancies (VO) or cations from active electrodes (Waser et al., 2009; Chen et al., 2013; Kamiya et al., 2014; Tang et al., 2015). However, due to the high mobility of VO and relative low endurance of cation-based resistive random-access memories (RRAM), it is a challenge to maintain stable intermediate states, which greatly limited the applications of memristors in multi-level RS and artificial synapses.

Compared to VO and cations from electrodes, another common ionic defect in metal oxides, cationic interstitial (Cint) can also contribute to the successful RS, which has been less focused on previously. In the limited reports, Cint has shown great potential in enhancing the performance of memristors with better stability and endurance, higher ON/OFF ratio, lower operation voltage, etc. Multi-level RS and synaptic RS have also been realized via modulating Cint in memristors. Hence, in this mini-review, we focused on studying the Cint-induced RS behaviors from the previous reports. Both theoretical and experimental works have been investigated, which may provide reference and inspiration for the rational design of multifunctional memristors from a new perspective and may shed some light on the increments in memristors.

REVIEW OF THE WORKS RELATED TO THE FIRST-PRINCIPLE STUDIES

First-principles calculations have been always employed to investigate the mechanism of the RS behavior through some calculations in terms of formation energy, the density of states, partial charge densities, etc. For Cint-induced RS, there are two main contributions from Cint to realize or enhance the RS: forming a conductive path and promoting charge transfer in the metal oxides. Related works have been summarized in Table 1.

Gu et al. have compared the formation possibility of conductive paths with Cu interstitials (Cu$_{int}$) and VO in the Ta$_2$O$_5$ atomic switch through first-principles studies (Gu et al., 2010): Figure 1A shows that Cu$_{int}$ can form an effective conduction channel in the Ta$_2$O$_5$, as the formation of Cu$_{int}$ may connect the two adjacent Ta-O planes through the simulation process, while VO failed to form such a conductive channel. But it should be noted that the conductive path formed by Cint is sensitive to the concentrations of interstitials, which need to be tuned carefully in the experiments.

The formation of the conductive path with Cint is sensitive to the valences of the doped cations as well. Li et al. have systematically calculated the TiO$_2$ and ZrO$_2$ with different Cint and investigated how Cint with different valence states may affect the transport coefficients (Li et al., 2015). Figure 1B illustrates the deformation electron densities for the TiO$_2$ with Cu$_{int}$, Ti$_{int}$, and Zr$_{int}$ respectively. The blue region around Cu$_{int}$ indicates that the loss of $e^-$ from Cu could form ionic bonds with nearby O atoms, while such a phenomenon has not been observed in the situation of Ti$_{int}$ and Zr$_{int}$. The calculation results indicate that the transport coefficients of the materials with Ti$_{int}$ and Zr$_{int}$ are higher than that with Cu$_{int}$. To optimize the RS behavior, the doping of metals with +4 or higher valences could be employed as it may enhance the transport properties.

Similarly, Zr$_{int}$ and Ti$_{int}$ in CeO$_2$ and Ta$_{int}$ in Ta$_2$O$_5$ have also been confirmed to contribute to the formation of conductive paths in memristor. As it is shown in Figure 1C, Ti$_{int}$ can form a more obvious conductive path in CeO$_2$ compared to the Ti substitution (Ti$_{sub}$). And then, Ti$_{int}$ and Zr$_{int}$ have been introduced in experiments and successfully improved the RS performance of CeO$_2$ RRAMs (Hussain et al., 2018). Zhu et al. compared the VO and Ta$_{int}$ in the Ta$_2$O$_5$-based RRAM and confirmed the contribution of Ta$_{int}$ in realizing RS under oxygen-poor conditions (Zhu et al., 2016). Thus, it is concluded that the Cint can introduce more defect states to above metal oxides than that of VO, and the Cint-induced RS can be enhanced under an electric field.

The synergistic effects of VO and Cint for achieving RS have also been identified in memristors. In the Au-doped HfO$_2$, it has been confirmed that both VO and Au$_{int}$ are involved in the formation of conductive filaments (Tan et al., 2018). Similarly, Abdelouahed et al. compared the TiO$_2$ with VO and Ti$_{int}$ and revealed the co-formation of both defects, which induced a net dipole moment, and enhanced RS behavior under an electric field (Abdelouahed and Mckenna, 2015).

REVIEW OF EXPERIMENTAL WORKS

Cint-induced or enhanced RS behavior in memristors has also been confirmed in experimental works (as summarized in Table 2).
The formation of Cints and Cint-induced RS behavior

The Cints can be introduced to metal oxides by modifying the synthesis parameters, such as the annealing conditions, oxygen partial pressure, doping concentration, etc. For example, by changing the annealing temperature and improving the oxygen concentration during the annealing process, Cuints have been successfully formed in the CuxO, and the RS can be enhanced by...

### TABLE 1 | Theoretical works on the Cint-induced RS behavior.

| Materials | Interstitials | Effects | Ref |
|-----------|--------------|---------|-----|
| Ta₂O₅     | Cuₙ₁       | Forming conductive path | Gu et al. (2010) |
| TiO₂      | Tiₙ₀ or Zrₙ₀ | Promoting charge transfer | Li et al. (2015) |
| CeO₂      | Tiₙ₀ or Zrₙ₀ | Forming conductive path | Hussain et al. (2018) |
| Ta₂O₅     | Taₙ₀       | Forming conductive path | Zhu et al. (2016) |
| HfO₂      | Alₙ₁ + Vo  | Forming filaments | Tan et al. (2018) |
| TiO₂      | Tiₙ₀ + Vo  | Forming net dipole moment | Abdelouahed and Mckenna, (2015) |

### FIGURE 1 | (A) Isosurface plot of the partial charge density corresponding to the defect state induced by the interstitial Cu₂₉ and Vo in Ta₂O₅ (reproduced with permission (Gu et al., 2010). Copyright 2010, American Chemical Society); (B) deformation electron density in [110] for the defected TiO₂ with the Cu₂₉, Ti₂₉, and Zr₂₉ (reproduced with permission (Li et al., 2015). Copyright 2015, Lei Li et al.); (C) isosurface plots of Ti₂₉ and Ti₁₂ (reproduced with permission (Hussain et al., 2018). Copyright 2018, Springer-Verlag GmbH Germany).

### TABLE 2 | Experimental works on the Cint-induced RS behavior.

| Materials | Interstitials | Cint forming conditions | Effects | Ref |
|-----------|--------------|-------------------------|---------|-----|
| CuxO      | Cu₂₉        | Annealing in Ar environment | Enhanced RS | Rehman et al. (2018) |
| ZnO       | Zn₂₉        | Sputtering under high oxygen partial pressure | Change bipolar (with O₂⁺) into unipolar (with Zn₂₉) RS | Wu et al. (2014) |
| ZnO      | Zn₂₉        | PLD, rapid thermal annealing | Change TGSC conductance (with Vo) into diode-like RS (with Zn₂₉) | Sekhar et al. (2015) |
| Al₂O₃     | Al₂₉        | Sol-gel, Ru, and Al co-doping | Improved stability, endurance, and ON/OFF ratio, lowered SET voltage | Li et al. (2014) |
| NiO:SnO₂  | Ru₂₉ + Al₂₉ | Depositing Ti as a buffer layer in CeO₂/TiSnO₂ | Improved stability, endurance, and ON/OFF ratio, lowered SET voltage | Rana et al. (2017) |
| CeO₂      | Ti₂₉       | Hydrothermally synthesized Mn-doped SnO₂ | Improved multi-level RS, improved stability and endurance | Xu et al. (2018) |
| TiO₂      | Ti₂₉ + Vo  | Thermally-induced self-doping and phase transformation | Improved stability, endurance, and ON/OFF ratio, lowered SET voltage | Hazra et al. (2021) |
| MoO₃      | Mo₂₉        | Hydrothermally synthesized hexagonal MoO₃ | Multi-level RS | Patil et al. (2021) |
| ZnO      | Zn₂₉ + Vo  | 2 wt% Cu-doped ZnO | Enhanced electric controlled RS and light-modulable RS | Saini et al. (2021) |
| TiO₂      | Ti₂₉ + Ag⁺ + K⁺ | Fabricate Ag/TiO₂-LPE/FTO device | Enhanced stability and endurance, lowered SET voltage, bipolar RS | Abbasi et al. (2020) |
| LaAlO₃    | B₂₉       | B-doped LaAlO₃ | Enhanced RS behavior, realized ferromagnetic ionic-electronic conductor | Park et al. (2018) |
tuning the Cu_{int} in the memristors (Rehman et al., 2018). In the sputtering process, by adjusting the oxygen partial pressure, the formation of O_{int} or Zn_{int} could be controlled, and interestingly, it is found that the bipolar and unipolar RS behavior can be tuned by forming O_{int} and Zn_{int} in the Al/ZnO/Al memory device, respectively (Wu et al., 2014). In the pulsed laser deposition (PLD), rapid thermal annealing may also change the defects in ZnO/Al2O3 memristor: the trap-controlled-space-charge (TCSC) limited conduction mechanism has been observed when Vo dominates, while, diode-like RS behavior has been identified in the case of Zn_{int} dominating. In the latter, the stability, endurance, and ON/OFF ratio of the memristor have been significantly improved as it is shown in Figure 2A (Sekhar et al., 2015). Such transition is ascribed to the formation of ZnAl2O4 as an interlayer, which acts as the e⁻ trapping/detrapping area and achieved successful RS.

In the memristors fabricated from solution-processed, C_{int}s are usually introduced via doping. In the NiO:SnO2 memristor, Ru_{int} and Al_{int} can be achieved through Ru and Al co-doping in the sol-gel process (Li et al., 2014). Compared to the Vo induced RS, the RS behavior conducted by Ru_{int} and Al_{int} could be greatly improved and show a larger ON/OFF ratio. The enhanced RS is ascribed to the increased trapped states between the equilibrium Fermi level and conduction band by Ru_{int} and Al_{int} (Li et al., 2014). Mn_{int}s have been achieved in SnO2 by increasing the Mn-doping level to 12.5 mol% in the liquid-liquid interface hydrothermal process and compared to the pure SnO2 with Vo, Mn-doped SnO2 memristor shows more effective and stable RS with significantly larger ON/OFF ratio and better intermediate state retention (Xu et al., 2018).

Adding a buffer layer is another method to introduce the C_{int}s. As it is illustrated in Figure 2B, Ti_{int}s have been introduced by a Ti buffer layer in the TaN/CeO2/Ti/CeO2/Pt memory device, in which Ti_{int}s assisted the formation of conductive filaments in CeO2. Compared to the device without the Ti buffer layer, the device’s stability and endurance could be significantly improved alongside the lower SET voltage and larger memory window (Rana et al., 2017). Similarly, by alternately depositing the SnO2 layer with Vo and Mn-doped SnO2 layer with Mn_{int}, Mn_{int}s have been introduced to the SnO2-based RRAMs, which significantly enhance the RS behavior with a higher ON/OFF ratio and better stability and endurance (Xu et al., 2017).

**C_{int}-induced Multi-level RS**

Multilevel RS has also been investigated in C_{int}-induced memristors. Intrinsic multi-state RS behavior with good endurance and stability has been observed in Mn-doped SnO2-based memristor by increasing the Mn-doping concentration, as it is illustrated in Figure 2C (Xu et al., 2018). By comparing the RS behavior of Mn-doping, Al-doping, and In-doping in SnO2 together with the XPS results and the calculated defect formation energies, the multi-level RS has been ascribed to Mn_{int} instead of Vo. Iodine interstitials induced multi-level RS has also been achieved in the Ag/CH3NH3PbI3/Pt cells as shown in Figure 2D (Choi et al., 2016). Owing to the relatively low activation energies, the migration of I_{int} enables filament formation and annihilation at a relative operation voltage.

**Synergistic RS induced by C_{int} and other defects**

Furthermore, the synergistic effect of C_{int}s with other ionic defects in memristor has been confirmed in experiments more
than the theoretical results above (Lee et al., 2021). The synergistic effect of Ti\textsubscript{int} with Vo has been confirmed in the Au/TiO\textsubscript{2} nanotube/Ti memory (Hazra et al., 2021). In the Ti/ MoO\textsubscript{3}/FTO memory cell, it is identified that Mo\textsubscript{int}, surface defects, and Vo have contributed together to the multilevel RS behavior (Patil et al., 2021). Zn\textsubscript{int} together with Vo enables the formation and rupture of conducting filaments in the Cu-doped ZnO, and both electric controlled and white light modulated RS has been achieved (Saini et al., 2021). Similarly, Vo and I\textsubscript{int} assisted RS via a Schottky barrier tuning has also been verified in the Au/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}/TiO\textsubscript{2}/FTO memory device (Lee et al., 2021).

In addition, C\textsubscript{int} can act as assistance or a game-changer in metal oxides. Figure 3A illustrates the defect-abundant memory device of Ag/TiO\textsubscript{2}-LPE (known as lime peel extract)/FTO, in which Ti\textsubscript{int} from TiO\textsubscript{2}, Ag\textsuperscript{+} oxidized from the Ag electrode, and K\textsuperscript{+} from the LPE synergistically contribute to the RS behavior. Ti\textsubscript{int} provides active paths for cation migrations, which enhanced the stability and endurance of bipolar RS of the memory cell with low operation voltage and high ON/OFF ratio (Abbasi et al., 2020). In the B-doped LaAlO\textsubscript{3}, B\textsubscript{mol}\textsubscript{5} realized charge injection into the neighboring cations, which enables remarkable electrical RS and transformed the oxide into a ferromagnetic ionic-electronic conductor at the same time, as it is shown in Figure 3B. This extends applications of C\textsubscript{int} to contribute to energy-efficient and spin-based devices (Park et al., 2018).

**SUMMARY AND OUTLOOK**

In summary, the cationic interstitials induced RS behavior in metal-oxide-based memories has been summarized. For a defect that has been less focused, there are very few reports on the formation, contribution, and mechanism of C\textsubscript{int}-induced RS behavior compared to those on Vo or active electrodes. However, from both theoretical and experimental aspects, the C\textsubscript{int}-induced or enhanced RS behavior has been confirmed in recent years. As discussed above, diversified C\textsubscript{int}s provide more opportunities to tailor the metal oxides for different electronic devices. The rational fabrication of memristors with C\textsubscript{int}s may give rise to remarkable enhancement in RS performance with better stability and endurance, lower operation voltage, higher ON/OFF ratio, faster device speed, etc. However, C\textsubscript{int}-based memristors are sensitive to the concentration and valence state of C\textsubscript{int}, which makes the formation of C\textsubscript{int} in metal oxide synthesis need to be carefully modulated. By adjusting the C\textsubscript{int}s, suitable electric structures would be established in the
metal oxides, which helps improve the performance of the electronic devices.

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All authors listed have made a substantial, direct, and intellectual contribution to the work, and approved it for publication.

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