Perovskite Nickelate Ionotronics for AI and Brain-Machine Interfaces

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Abstract

Human brain is the ultimate computing machine in nature. Creating brain-like devices that emulate how the brain works and can communicate with the brain is crucial for fabricating highly efficient computing circuits, monitoring the onset of diseases at early stages, and transferring information across brain-machine interfaces. Simultaneous transduction of ionic-electronic signals would be of particular interest in this context since ionic transmitters are the means of information transfer in human brain while traditional electronics utilize electrons or holes. In this perspective, we propose strongly correlated oxides (mainly focused on perovskite nickelates) as potential candidates for this purpose. The capability of reversibly accepting small ions and converting ionic signal to electrical signals renders perovskite nickelates strong candidates for neuromorphic computing and bioelectrical applications. We will discuss the mechanism behind the interplay between ionic doping and the resistivity modulation in perovskite nickelates. We will also present case studies of using the perovskite nickelates in neuromorphic computing and brain-machine interface applications. We then conclude by pointing out the challenges in this field and provide our perspectives. We hope the utilization of strong electron correlation in the perovskite nickelates will provide exciting new opportunities for future computation devices and brain-machine interfaces.

Key words: Perovskite nickelate; Metal to insulator transition; Ionic doping; Brain-like computation; Brain-machine interface

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1 Introduction

The brain is the most delicate computing machine in nature that is capable of processing complex visual, aural, olfactory, and haptic information. It is made of a complicated neural network, consisting of around 10^{11} neurons connected by 10^{14} to 10^{15} synapses.[1–4] The brain can perform over 10^{16} operations per second, which is more powerful than modern supercomputers, but at the same time only consumes 20 Watt of energy.[5–7] This led to tremendous research interest in the brain over the past several decades in understanding how brain works and creating computing devices that emulate the brain. For example, in the field of brain-inspired computing, both algorithms and hardware are being developed to take advantage of the high computing efficiency of the neural network. For hardware implementation, various efforts have been devoted to constructing neuromorphic devices (artificial synapses and neurons) with traditional CMOS technology or emerging materials such as redox, phase change, ferroelectric, and magnetic materials.[8–10] Another exciting line of research lies in the field of brain-machine interface (BMI) that tries to probe brain circuits with high spatial and temporal precision to understand how the brain works, and later use such mechanism to control prostheses and restore mobility and sensations for severely disabled patients. Fabrication of such devices requires multifunctional materials that can accept ionic signal from the brain circuits and then convert it to electronic signal that modern electronic devices can process.

In this short perspective, we highlight recent progress in the ionic doping of perovskite nickelates and its consequential resistivity modulation, i.e., ionotronics, for applications in brain-inspired computing and BMIs, as schematically shown in Fig. 1. The lattice of perovskite nickelate is highly tolerant to ionic dopant and H doping results in a room temperature metal to insulator transition (MIT).[11] Such band filling induced Mott MIT shows several key benefits in constructing artificial neural networks: 1) The strongly correlated electrons in the perovskite nickelate lead to as high as 10 orders of magnitude change in resistance during the MIT. 2) Proton is the lightest element in the periodic table and inherently possess the possibility for ultrafast devices. 3) Due to its small size, the proton has various metastable states in the nickelate lattice and provides the potential in fabricating reconfigurable neuromorphic devices. Besides the neuromorphic devices, the perovskite nickelates also demonstrate key advantages for BMI applications: 1) perovskite nickelates can be doped with small ions, e.g., H^+, Na^+ and Mg^+ etc., which are the same in-

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formation transmitters in the brain, as shown on the top part of Fig. 1. Such ionic doping modulates the band structure of perovskite nickelates and results in largely amplified response in their electrical resistivity through the Mott MIT.[11,12] 2) Perovskite nickelates are robust and function well in biological liquid media.

In the following sections, we will start with the mechanism of ionotronics in perovskite nickelates and then briefly discuss recent progress of their applications in neuromorphic devices and BMIs.

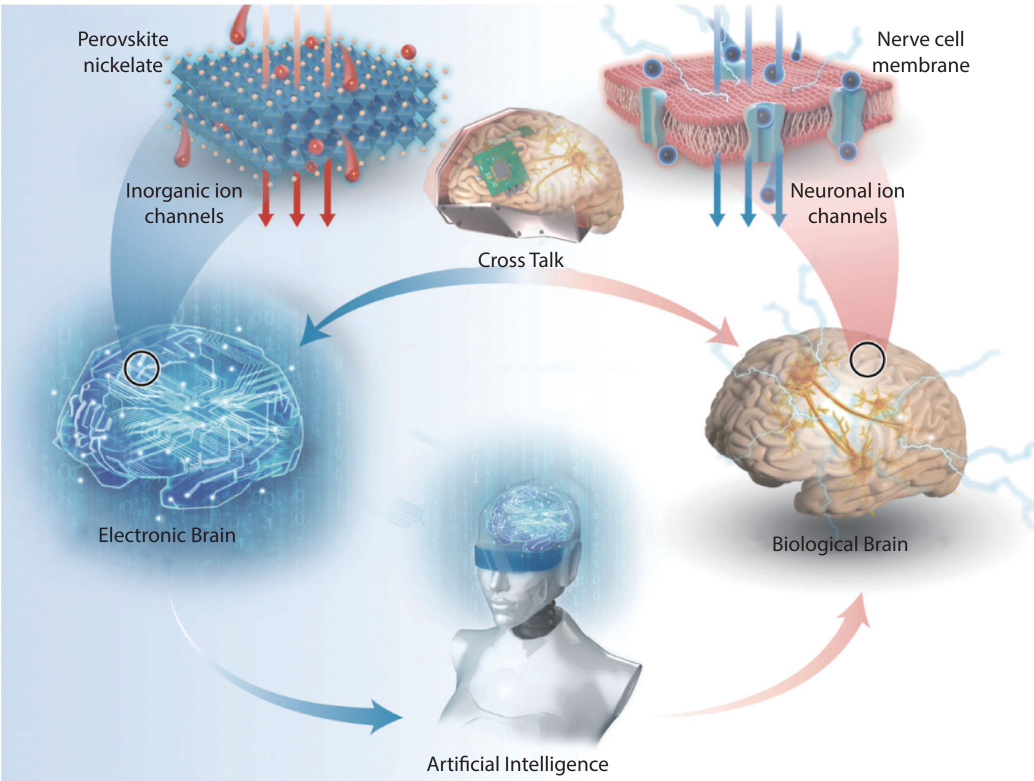

Fig. 1 Perovskite nickelates for AI and brain-machine interfaces (BMIs).

Perovskite nickelates are characterized by their strongly correlated d-orbital electrons and consequential metal to insulator transition. Ion-electronic doping in the nickelate lattice is an effective way to modulate the device resistance of artificial synapses and artificial neurons. Since small ions can flow in both the perovskite nickelates and the biological neural cells, nickelate devices can serve as the bridge across the BMI.

2 Ion doping and the metal to insulator transition

Transformative technologies require emerging materials and new fabrication strategies.[1,13–18] The perovskite nickelates exhibit multiple electronic phase transitions associated with the variations in d-band related orbital configurations and occupations. Their conventional MIT is owing to the charge disproportionation (or anti-disproportionation) of the valance of Ni^{3+} based configuration (e.g., $Ni^{3+} \leftrightarrow Ni^{3\pm\Delta}$) as can be triggered by critical temperature (TMIT) or pressure (PMIT).[19] As a result, their electron transport behaviors show transitions between metals and semiconductors as manifested by the different temperature dependence in resistivity. The magnitude in TMIT is mainly determined by the rare-earth composition occupying the A-site of the perovskite structure (ABO_3) and can be adjusted within a broad range of temperatures of 100-600 K.[20] For example, enlarging the ionic radius of the rare-earth element results in less distorted NiO_6 octahedron to strengthen metallic phase, and as a result the TMIT is reduced. In addition, the TMIT can be also slightly adjusted via establishing interfacial strain or via electron accumulation.[19]

Apart from the conventional MIT, hydrogen (or lithium and magnesium) doping and associated electron filling changes the orbital configuration of Ni and triggers electronic phase transition from the Ni^{3+} to Ni^{2+} configuration.[21] The enlarged orbital occupancy in e_g (e.g., filling the previous empty state) results in stronger Coulomb repulsions among the itinerant electrons and electron localizations, and triggers the formation of a highly insulating phase.[21] Furthermore, there are numerous metastable states for H in the perovskite nickelate lattice which leads to distinct electrical properties. Therefore, delicate control of the H concentration and H distribution can lead to multiple neural functions for brain-inspired computation.[22] Technically, the hydrogenation process can be either chemically performed via annealing in hydrogen atmosphere[21] or electrochemically triggered by imparting electric field within electrolytes.[23]

3 Application in brain-like computation

It is a lon-stangding dream to build a computer which can work like the human brain.[24] To achieve brain-like computing, the key is to simulate the behaviors of synapses and neurons, which are the fundamental elements of a human neural system.[10] Perovskite nickelate devices can imitate human nervous system from both structural and functional aspects. The top and bottom electrodes can be thought of as the pre-neuron and post-neuron respectively. Besides, the electrical conductance of the thin film material can represent the weight of the synapse.[25] Based on the ion-electronic doping mechanisms, the distribution and local concentration of protons,[26,27] which significantly influence the resistance of nickelate devices, can be subsequently modulated with electric fields applied to the electrode.[18,28] These properties make it possible to simulate the learning enhancement and forgetting decline processes of synapses, i.e., potentiation and depression, in the human brain under the regulation of applied pulse signals. Relevant studies have also proven that hydrogen-doped nickelate devices are able to show non-volatile memory and history-dependent analogue-like states, which are two elemental characteristics for synapse-simulating devices.[29,30] In addition to the simulation of synapse, a perovskite nickelate device can be transformed among multiple neuromorphic functions such as memcapacitor, synapses and neurons.[22] A grow when required framework is developed based on such reconfigurable neural functions and shows excellent performance for tasks with incremental learning scenarios. This realization of multiple neural functions the same material can reduce the complexity of AI circuit design for power and space efficient computations. Besides, it is reported that after annealing in an extreme reducing atmosphere at low temperature, superconductive phase was found in oxygen reduced Sr-doped infinite layer of nickelate $R_{1-x}Sr_xNiO_2$.[7,31] These unique properties provide more research space for the application of rare earth perovskite nickelates in brain-like computing.

4 Application in brain-machine interface

BMIs require multi-disciplinary expertise among neurophysiology, materials science, and electrical engineering, aiming to build real-time connections between living brains and machines,[32] and finally to create new therapies to restore mobility and sensations to severely disabled patients, such as the patients with Alzheimer's disease and Amyotrophic lateral sclerosis (ALS).[33,34] As discussed earlier, the ion-based working mechanism for perovskite is similar to that in the brain which is the biggest advantage of perovskite nickelate to achieve BMIs. In a perovskite nickelate device, the redistribution of H ions modulates its resistance, and the device can serve as an interface to process ionic signal from biological world.[35] Besides, this device is stable in biological liquid media and non-toxic to living organisms.[36] Therefore, compared with the traditional silicon-based BMI implementation, it has better bio-integration potential. Recently, perovskite nickelates have been used to sense neurotransmitter release from the mouse brain, and both ex-vivo and in-vivo experiments have been reported.[36,37] Through interfacing the nickelate devices with an acute mouse brain slice or a live mouse brain, the release processes of dopamine and glutamate upon electrical stimulation were studied. These results demonstrate the application prospect of perovskite nickelates in the BMI field.

5 Conclusions

While utilization of the ionic-electronic phase transitions in perovskite nickelates provides fresh opportunities in exploring neuromorphic computing and BMI devices, several challenges still remain. First, the hydrogen ions have more than 100 metastable states in the nickelate lattice,[22] and each of them may have diverse effects on the electrical properties of the perovskite nickelates. Understanding such complex dynamic ion-electron correlation effects at room temperature requires continuous development in new computation methods beyond the ground state, such as dynamic mean-field theory (DMFT) calculations and ab-initio molecular dynamics (AIMD). Currently, most of the perovskite-nickelate-based neuromorphic computing devices are not fabricated at the circuit level. Developing large-scale circuit itself is challenging because it requires many fabrication processes and optimization. It will also be important to develop relevant setups to test the circuits and then interface them with AI software to perform real-world tasks. For the BMIs, interdisciplinary approaches are highly demanded, and only tight collaborations among neuroscientist, material scientists, electrical engineers and computer scientist can sprout alpha-version of devices. All these tasks are quite challenging but worthwhile. Our profound hope is to make highly efficient and complicated artificial neural circuits that one day can be conversely used to understand the origin of brain diseases, as well as to augment the biological brain.

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Conflict of interest

The authors declare no conflict of interest.

REFERENCES

1. S. Ramanathan, *MRS Bulletin*, 2018, 43, 534
2. Y. Tuchman, T. N. Mangoma, P. Gkoupidenis, Y. van de Burgt, R. A. John, N. Mathews, S. E. Shaheen, R. Daly, G. G. Malliaras, A. Salleo, *MRS Bulletin*, 2020, 45, 619
3. W. Zhang, B. Gao, J. Tang, P. Yao, S. Yu, M. F. Chang, H. J. Yoo, H. Qian, H. Wu, *Nature Electronics*, 2020, 3, 371
4. D. Marković, A. Mizrahi, D. Querlioz, J. Grollier, *Nature Reviews Physics*, 2020, 2, 499
5. P. Ball, *Nature*, 2012, 492, 176
6. Ray Kurzweil, *The Age of Spiritual Machines: When Computers Exceed Human Intelligence*, Penguin Books, England, 1999.
7. Z. Zhang, Y. Sun, H.-T. Zhang, *Journal of Applied Physics*, 2022, 131, 120901
8. F. Pan, S. Gao, C. Chen, C. Song, F. Zeng, *Materials Science and Engineering: R: Reports*, 2014, 83, 1
9. Z. Wang, H. Wu, G. W. Burr, C. S. Hwang, K. L. Wang, Q. Xia, J. J. Yang, *Nature Reviews Materials*, 2020, 5, 173

10. H.-T. Zhang, P. Panda, J. Lin, Y. Kalcheim, K. Wang, J. W. Freeland, D. D. Fong, S. Priya, I. K. Schuller, S. K. R. S. Sankaranarayanan, K. Roy, S. Ramanathan, *Applied Physics Reviews*, 2020, 7, 011309
11. J. Shi, Y. Zhou, S. Ramanathan, *Nature Communications*, 2014, 5, 4860
12. Y. Sun, M. Kotiuga, D. Lim, B. Narayanan, M. Cherukara, Z. Zhang, Y. Dong, R. Kou, C.-J. Sun, Q. Lu, I. Waluyo, A. Hunt, H. Tanaka, A. N. Hattori, S. Gamage, Y. Abate, V. G. Pol, H. Zhou, S. K. R. S. Sankaranarayanan, B. Yildiz, K. M. Rabe, S. Ramanathan, *Proceedings of the National Academy of Sciences*, 2018, 115, 9672
13. X. Zhang, *Materials Research Letters*, 2020, 8, 49
14. N. A. Spaldin, R. Ramesh, *Nature Materials*, 2019, 18, 203
15. L. Lou, Y. Li, X. Li, H. Li, W. Li, Y. Hua, W. Xia, Z. Zhao, H. Zhang, M. Yue, X. Zhang, *Advanced Materials*, 2021, 33, 2102800
16. G. Huang, X. Li, L. Lou, Y. Hua, G. Zhu, M. Li, H.-T. Zhang, J. Xiao, B. Wen, M. Yue, X. Zhang, *Small*, 2018, 14, 1800619
17. X. Li, L. Lou, W. Song, Q. Zhang, G. Huang, Y. Hua, H.-T. Zhang, J. Xiao, B. Wen, X. Zhang, *Nano Letters*, 2017, 17, 2985
18. H.-T. Zhang, Z. Zhang, H. Zhou, H. Tanaka, D. D. Fong, S. Ramanathan, *Advances in Physics: X*, 2019, 4, 1523686
19. G. Catalan, *Phase Transitions*, 2008, 81, 729
20. J. Chen, H. Hu, J. Wang, T. Yajima, B. Ge, X. Ke, H. Dong, Y. Jiang, N. Chen, *Materials Horizons*, 2019, 6, 788
21. Y. Zhou, X. Guan, H. Zhou, K. Ramadoss, S. Adam, H. Liu, S. Lee, J. Shi, M. Tsuchiya, D. D. Fong, S. Ramanathan, *Nature*, 2016, 534, 231
22. H.-T. Zhang, T. J. Park, A. N. M. N. Islam, D. S. J. Tran, S. Manna, Q. Wang, S. Mondal, H. Yu, S. Banik, S. Cheng, H. Zhou, S. Gamage, S. Mahapatra, Y. Zhu, Y. Abate, N. Jiang, S. K. R. S. Sankaranarayanan, A. Sengupta, C. Teuscher, S. Ramanathan, *Science*, 2022, 375, 533
23. Z. Zhang, D. Schwanz, B. Narayanan, M. Kotiuga, J. A. Dura, M. Cherukara, H. Zhou, J. W. Freeland, J. Li, R. Sutarto, F. He, C. Wu, J. Zhu, Y. Sun, K. Ramadoss, S. S. Nonnenmann, N. Yu, R. Comin, K. M. Rabe, S. K. R. S. Sankaranarayanan, S. Ramanathan, *Nature*, 2018, 553, 68
24. P. A. Merolla, J. V. Arthur, R. Alvarez-Icaza, A. S. Cassidy, J. Sawada, F. Akopyan, B. L. Jackson, N. Imam, C. Guo, Y. Nakamura, B. Brezzo, I. Vo, S. K. Esser, R. Appuswamy, B. Taba, A. Amir, M. D. Flickner, W. P. Risk, R. Manohar, D. S. Modha, *Science*, 2014, 345, 668
25. S. Choi, J. Yang, G. Wang, *Advanced Materials*, 2020, 32, 2004659
26. I. A. Zaluzhnyy, P. O. Sprau, R. Tran, Q. Wang, H.-T. Zhang, Z. Zhang, T. J. Park, N. Hua, B. Stoychev, M. J. Cherukara, M. V. Holt, E. Nazaretski, X. Huang, H. Yan, A. Pattammattel, Y. S. Chu, S. P. Ong, S. Ramanathan, O. G. Shpyrko, A. Frano, *Physical Review Materials*, 2021, 5, 095003
27. U. S. Goteti, I. A. Zaluzhnyy, S. Ramanathan, R. C. Dynes, A. Frano, *Proceedings of the National Academy of Sciences*, 2021, 118, e2103934118
28. C. Oh, M. Jo, J. Son, *ACS Applied Materials & Interfaces*, 2019, 11, 15733
29. J. Shi, S. D. Ha, Y. Zhou, F. Schoofs, S. Ramanathan, *Nature Communications*, 2013, 4, 2676
30. H.-T. Zhang, T. J. Park, I. A. Zaluzhnyy, Q. Wang, S. N. Wadekar, S. Manna, R. Andrawis, P. O. Sprau, Y. Sun, Z. Zhang, C. Huang, H. Zhou, Z. Zhang, B. Narayanan, G. Srinivasan, N. Hua, E. Nazaretski, X. Huang, H. Yan, M. Ge, Y. S. Chu, M. J. Cherukara, M. V. Holt, M. Krishnamurthy, O. G. Shpyrko, S. K. R. S. Sankaranarayanan, A. Frano, K. Roy, S. Ramanathan, *Nature Communications*, 2020, 11, 2245
31. D. Li, K. Lee, B. Y. Wang, M. Osada, S. Crossley, H. R. Lee, Y. Cui, Y. Hikita, H. Y. Hwang, *Nature*, 2019, 572, 624
32. M. A. Lebedev, M. A. L. Nicolelis, *Physiological Reviews*, 2017, 97, 767
33. M. J. Vansteensel, E. G. M. Pels, M. G. Bleichner, M. P. Branco, T. Denison, Z. V. Freudenburg, P. Gosselaar, S. Leinders, T. H. Ottens, M. A. van den Boom, P. C. van Rijen, E. J. Aarnoutse, N. F. Ramsey, *the New England Journal of Medicine*, 2016, 375, 2060
34. S. Battistoni, V. Erokhin, S. Iannotta, *Neural Plasticity*, 2017, 2017, 6090312
35. P. C. Harikesh, C.-Y. Yang, D. Tu, J. Y. Gerasimov, A. M. Dar, A. Armada-Moreira, M. Massetti, R. Kroon, D. Bliman, R. Olsson, E. Stavrinidou, M. Berggren, S. Fabiano, *Nature Communications*, 2022, 13, 901
36. H.-T. Zhang, F. Zuo, F. Li, H. Chan, Q. Wu, Z. Zhang, B. Narayanan, K. Ramadoss, I. Chakraborty, G. Saha, G. Kamath, K. Roy, H. Zhou, A. A. Chubykin, S. K. R. S. Sankaranarayanan, J. H. Choi, S. Ramanathan, *Nature Communications*, 2019, 10, 1651
37. Y. Sun, T. N. H. Nguyen, A. Anderson, X. Cheng, T. E. Gage, J. Lim, Z. Zhang, H. Zhou, F. Rodolakis, Z. Zhang, I. Arslan, S. Ramanathan, H. Lee, A. A. Chubykin, *ACS Applied Materials & Interfaces*, 2020, 12, 24564

Biography

Hai-Tian Zhang is currently a professor in the School of Materials Science and Engineering at Beihang University, Beijing, China. He received his Ph.D. degree in Materials Science and Engineering in 2018 from Pennsylvania State University while working at the Nanoscale Science Materials Research Science and Engineering Center (MRSEC). He was then awarded the Gilbreth Research Fellowship in 2018 to carry out research work in the School of Engineering at Purdue University. After being elected for National High-level Young Talent Program of China, he joined Beihang University in 2021. His current research interest is mainly focused on utilizing ordered microstructures to tune the electrical and magnetic properties of functional materials for applications such as brain-inspired computing, magnetic devices, and sensors. Hai-Tian Zhang has published 35 peer-reviewed papers in *Science, Nature Mater., Nature Commun., Adv. Mater., Adv. Func. Mater., Nano lett.* etc. and has been authorized 1 U.S. patent.