

Proton-Tunable Analog Transistor Using a Coordination Polymer

Mark D. Allendorf, Elliot J. Fuller, Donald A. Robinson, D. Catalin Spataru,
Vitalie Stavila, A. Alec Talin, *Sandia National Laboratories, Livermore, CA USA*

Artificial neural networks (ANN), an alternative to digital logic, can supersede Moore's law limitations, solve complex non-numeric problems, and are compatible with low-power analog hardware that can reduce energy consumption. Analog devices emulating nerve synapses offer an alternative to digital logic for ANN. Ion-based switches, such as memristors, could potentially address these challenges. However, correlated ion and charge transport in their conducting channels and numerous issues with the switching materials are a barrier to development and optimization of these potentially revolutionary concepts. Recently, Talin and coworkers developed a novel three-terminal redox transistor (RT)¹ based on conducting organic polymers (PEDOT:PSS) that can overcome the inherent limitations of two-terminal memristors for ANN and low-power computing (Fig. 1). Dozens to hundreds of conducting states are feasible, with fast switching and much lower switching voltages than CMOS transistors. They also demonstrated that these polymer redox transistors endure $>10^9$ 'read-write' operations and project that switching times <100 ns are feasible.²

Gaining fundamental insight into the performance-controlling phenomena in ion-based switches such as the RT is difficult because ionic and electronic charge transport are correlated in these devices. In the RT, the complex morphology of the polymer electrodes, which have both ordered and disordered regions resembling "cooked spaghetti"³

affects the density of states (DOS), leading to carrier concentration-dependent mobilities.⁴ Consequently, disentangling the correlated effects of morphology, composition, and device architecture requires new synthetic approaches, much greater control over disorder, and operando experimental probes that can generate spatially resolved potentials and composition and microstructural maps.

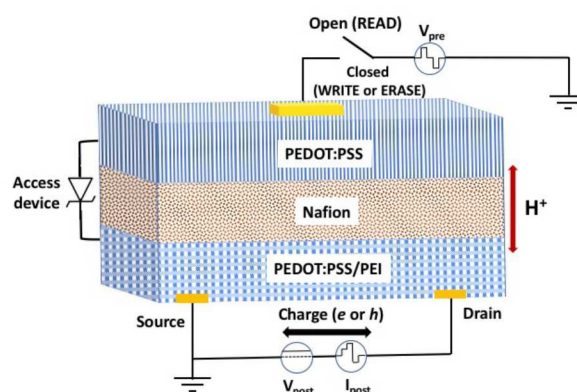


Figure 1. Proton transistor architecture. Gate (top) and channel (bottom) electrodes are separated by an electrolyte layer transporting ions/protons (Ref. 1).

We are developing self-assembled nanoporous materials (SNM) as a new class of mixed conductors to enable independent control of ion and electronic charge transport. SNM offer unprecedented control over porosity to confine and rapidly transport ions, as well as long-range order and synthetic versatility to tailor electronic conductivity. In this presentation we will discuss the requirements for such materials, in particular, highlighting the potential of nanoporous framework materials to provide tailorable pore dimensions with chemical functionalities and redox behavior suitable for ion-based switching. As a starting point for determining structure-function relationships, we are considering redox-active MOFs, which can provide tunable electrical conductivity and fast ion transport combined with a structure having long-range order. An experimental device incorporating these materials will be described to illustrate the potential for use of MOFs in RT devices. Fabrication methods and device assembly will be described. Data from operando measurements of local composition within the conducting channel (via Raman microscopy) and state-of-charge maps obtained from UV-vis spectroscopy will be presented with maps showing the effects of local morphology on conductivity to create a detailed picture of material and device performance. Results from analytical modeling will be compared with these experimental to determine the validity of current models to describe the coupled ion and charge transport.

- (1) van de Burgt, Y.; Lubberman, E.; Fuller, E. J.; Keene, S. T.; Faria, G. C.; Agarwal, S.; Marinella, M. J.; Talin, A. A.; Salleo, A. A non-volatile organic electrochemical device as a low-voltage artificial synapse for neuromorphic computing. *Nat. Mater.* **2017**, *16* (4), 414.
- (2) Fuller, E. J.; Keene, S. T.; Melianas, A.; Wang, Z.; Agarwal, S.; Li, Y.; Tuchman, Y.; James, C. D.; Marinella, M. J.; Yang, J. J. et al. Parallel programming of an ionic floating-gate memory array for scalable neuromorphic computing. *Science* **2019**, *364*, 570.
- (3) Noriega, R.; Rivnay, J.; Vandewal, K.; Koch, F. P. V.; Stingelin, N.; Smith, P.; Toney, M. F.; Salleo, A. A general relationship between disorder, aggregation and charge transport in conjugated polymers. *Nat. Mater.* **2013**, *12* (11), 1038.
- (4) Friedlein, J. T.; Rivnay, J.; Dunlap, D. H.; McCulloch, I.; Shaheen, S. E.; McLeod, R. R.; Malliaras, G. G. Influence of disorder on transfer characteristics of organic electrochemical transistors. *Appl. Phys. Lett.* **2017**, *111* (2).