Electronic Supplementary Information

Negative Differential Resistance and Hysteresis in Au/MoO₃₋δ/Au Devices

Dmitri Kalaev[1,*], Avner Rothschild[2], Ilan Riess[1,*]

[1] Physics Department, Technion-IIT, Haifa, 3200003, Israel
[2] Materials Science and Engineering Department, Technion-IIT, Haifa, 3200003, Israel

E-mail: dkalaev@mit.edu, riess@technion.ac.il

Keywords: negative differential resistance, hysteresis, MIM, MIEC, oxygen vacancies

1. Theory

The analysis of the *I-V* relation and their dependence on frequency and temperature follows the previously published theoretical method which refers to devices based on mixed-ionic-electronic-conductors (MIECs).[1,2] The MIEC conducts singly charged donors and electrons. The electrons propagate as small polarons.[3] A single reversible reaction is allowed in the model, that of donor ionization (oxygen vacancy ionization/recombination),

$$e' + V_O^{\bullet} \leftrightarrow V_O^{\times} \tag{1}$$
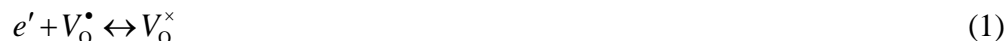
using Kröger-Vink notation for point defects. When the reaction is in local equilibrium the corresponding mass action law is,

$$K n \cdot N_D = N_\times \tag{2}$$

where K is the reaction constant, n, N_D and $N_\times$ are electron, charged and neutral donor concentrations, respectively. The electron concentration calculated under local equilibrium and flat bands is denoted as n_0. The relative thick, bulk tends towards local neutrality.[4] n_0 is a fitting

1

parameter. Under varying voltage, as under triangular voltage cycles (TVC), the reaction may be far from equilibrium.

Both the electrons and the oxygen vacancies move under an applied driving force by drift and diffusion. For samples of thickness beyond a few nm the linear drift-diffusion equations hold.[5] The current density equation under the dilute concentration approximations, is for electrons,

$$j_e = k_B T v_e \partial_x n + q v_e E \cdot n \tag{3}$$

and for the mobile donors $V_O^{\bullet}$,

$$j_i = -k_B T v_i \partial_x N_D + q v_i E \cdot N_D \tag{4}$$

where $\partial_x = \partial/\partial x$, q - denotes elementary charge, k_B – the Boltzmann constant, j - current density, v - mobility and E - electric field. It is important to emphasize that the mobility of the ions is constant, and so is the mobility of the electrons. v_e and v_i are fitting parameters. The Poisson equation, for the one dimensional configuration, is,

$$\partial_x E = q \left(\varepsilon_0 \varepsilon_r \right)^{-1} \left(N_D - n \right) \tag{5}$$

where ε_0 is the vacuum permittivity and ε_r is the dielectric constant of MoO$_{3-\delta}$.

Time dependence is introduced via the continuity equations. The one for electrons is,

$$\partial_x j_e = q \partial_t n - q G_e \tag{6}$$

for charged donors,

$$\partial_x j_i = -q \partial_t N_D + q G_i \tag{7}$$

and for the immobile neutral donors $V_O^{\times}$,

$$0 = -\partial_t N_\times + G_\times \tag{8}$$

The source terms in equations (6)-(8) are related,

$$G_\times = -G_e = -G_i \tag{9}$$

They originate from reaction (1),

$$G_{\times} = \tau^{-1} \left(K n N_{\mathrm{D}} - N_{\times} \right) \tag{10}$$

where τ is the relaxation time of that reaction.

Equations (2)-(10) describe the Au/MoO$_{3-\delta}$/Au system including the time dependent, non-steady state behavior. There are six unknowns: n, N_D, $N_{\times}$, E, j_e, j_i and six equation where five of the equations contain a first order derivative with respect to position x. Thus additional five boundary values are required. Because of the derivative with respect to time the initial state of the relevant parameters has also to be known.

Two boundary conditions are the electron concentrations, n_{left} and n_{right}, at the oxide boundary. and in the present arrangement they are equal. $n_{\mathrm{left}} = n_{\mathrm{right}}$ are fitting parameters.

The second pair of constraints is given by the chemical potential of the neutral donors in the surroundings, expressed by their effective concentration $N_{\times,\mathrm{left}}^{\mathrm{out}}$ and $N_{\times,\mathrm{right}}^{\mathrm{out}}$.[1] The effective concentration is defined as the concentration of neutral donors, $V_{\mathrm{O}}^{\times}$, in the bulk when under equilibrium with the ambient oxygen. For a uniform atmosphere they are equal. $N_{\times,\mathrm{left}}^{\mathrm{out}} = N_{\times,\mathrm{right}}^{\mathrm{out}}$ are fitting parameters. Their impact comes through the ion current at the electrodes which follows a Butler-Volmer type relation.[4,6]

$$j_{\mathrm{i,contact}} = j_0 \left(e^{\frac{q\delta V_{\mathrm{th}}}{2k_{\mathrm{B}}T}} - e^{-\frac{q\delta V_{\mathrm{th}}}{2k_{\mathrm{B}}T}} \right) \tag{11}$$

where j_0 is an exchange current density at the corresponding electrode; The two exchange current densities, $j_{0,\mathrm{left}}$ and $j_{0,\mathrm{right}}$ are fitting parameters. δV_{th} - the drop in the Nernst voltage on an electrode,

$$\delta V_{\mathrm{th}} = -\Delta\mu_{\times}/zq \tag{12}$$

where μ_x is the chemical potential of the neutral donors, is assumed to appear on the electrode/MIEC interface.

The fifth boundary condition is the applied voltage given by,

$$V = -\frac{k_{\mathrm{B}}T}{q}\ln\left(\frac{n_{\mathrm{right}}}{n_{\mathrm{left}}}\right) - \int_{x_{\mathrm{left}}}^{x_{\mathrm{right}}} E dx \xrightarrow[n_{left}=n_{right}]{} - \int_{x_{\mathrm{left}}}^{x_{\mathrm{right}}} E dx \tag{13}$$

where x_{left} and x_{right} are the position of the edges of the trimmed oxide (*i.e.* the bulk without the narrow accumulation regions). The MoO$_{3-\delta}$/Au contacts are low resistance ohmic for electron transfer, thus V in equation (13) equals the applied voltage.

The initial condition is determined by the equilibrium state under zero voltage and uniform ambient, thus vanishing currents, and is given by the corresponding concentrations of the electrons and oxygen vacancies. The initial state can be solved numerically or by an analytic approximation.[7] For the flat band case the answer is straightforward with uniform electron and vacancy distributions.

2. Choosing fitting parameters of the model for the Au/MoO$_{3-\delta}$/Au device

The theory mentioned above is applied to the experimental results of 66. 1 to yield the parameters of the corresponding device. The fitted parameters for the measurements at 70 °C are summarized in Table 1 under device A. The *I-V* curves shown in Fig. 6, which depend on temperature, yield activation energies. One additional set of *I-V* relations measured on another device on the same assembly is shown in Fig. S1. These *I-V* relations are very similar to the ones in Fig. 6. The fitted parameters are summarized in Table 1 under device B. It is apparent that activation energies are the same for the two devices which indicates that the mechanisms are the same, as expected. The characteristic electron concentration, n_0, is different by less than a factor of two. This difference

we allocate to the different history of the two devices. Device A underwent longer tests until the final tests were done and thus lost slightly more oxygen, as can be inferred from Fig. 5. On sample B no long measurements were performed.

For fitting, first the dielectric constant was measured by ac impedance in the frequency range 10^2-10^5 Hz. The result $\varepsilon_r = 19$ is consistent with $\varepsilon_r = 18$ previously measured by Deb *et al.*[8] The dielectric constant is insensitive to temperature changes up to 80 °C. It is assumed that the dielectric constant is the same in the lower frequency range 10^{-4}-10^{-1} Hz.

The following parameters were determined by best fit: $n_0 = n_{\text{left}} = n_{\text{right}}$, $\alpha \equiv v_e / v_i$, K, $N_{x,\text{left}}^{\text{out}} = N_{x,\text{right}}^{\text{out}}$, $j_{0,\text{left}} = j_{0,\text{right}}$, τ. The fitting took advantage of known constraints as explained below. From those parameters the following ones were calculated: v_e, $\sigma_e = q v_e n_0$, v_i, $D_i = k_B T v_i / q$, δ and $\lambda_D = \left(\varepsilon_r \varepsilon_0 k_B T / q^2 n_0 \right)^{1/2}$.

The *I-V* relations are most sensitive to the characteristic electron concentration, n_0, and to the ratio $\alpha = v_e / v_i$. K is chosen to allow almost complete ionization of the vacancy so that $N_x \ll n_0, N_D$. The *I-V* relations are not sensitive to the exact values of K, $N_{x,\text{left}}^{\text{out}}$ and $N_{x,\text{right}}^{\text{out}}$. The relaxation time τ in Equation (10) is chosen to allow fast electron-donor recombination. The fitting is quite insensitive to this parameter.

The Au electrodes allow some exchange of the oxygen with the ambient. However the latter process is significant only in long measurements, as shown in Fig. 5. Thus the exchange current densities, $j_{0,\text{left}} = j_{0,\text{right}}$, where chosen low to simulate almost material blocking electrodes.

The deviation from stoichiometry δ of the oxide $MoO_{3-\delta}$ is calculated using the electron concentration n_0 which by local neutrality $(n_0 = N_D)$ equals the total oxygen vacancy concentration (as $N_x \ll N_D$). δ was controlled by the oxygen partial pressure during oxide deposition. While the electron conductivity σ_e was fitted to the *I-V* curve its validity was double checked against the one measured under low (10mV) triangular-voltage-cycles (TVC) by dV/dI.

The fitted ion mobility is $\nu_i \sim 10^{-12}$ cm^{2}V^{-1}s^{-1} at 70 °C. This is almost seven orders of magnitude lower than the mobility of the electrons, $\alpha = \nu_e/\nu_i = 4.75 \times 10^6$. Yet for slow changing voltage, the ion mobility has a significant impact on the device properties, resulting in hysteresis, as shown in Figs. 1, 4-6 and S1. The ion mobility, ν_i, when extrapolated to room temperature, using the activation energy $E_{a,\nu_i} = 0.9$ eV, reduces to 1.7×10^{-14} cm^{2}V^{-1}s^{-1}. This value is of the order of the vacancy mobility at room temperature determined by Aoki *et al.*[9] for amorphous GaO_x, $\nu_i \sim 7 \times 10^{-15}$ cm^{2}V^{-1}s^{-1}.

3. Effect of temperature on the *I-V* relations

Device B was tested in the temperature range 55-75 °C. The first measurement was done at 75 °C, then the temperature was decreased for the following measurement by 2.5 °C degrees. The *I-V* relations were measured for a scan rate of 5×10^{-4} V/s. To minimize stoichiometric changes only three cycles were allowed at each temperature and then the latter was lowered. The measured *I-V* relations are shown in Fig. S1a and the theoretical fit in Fig. S1b. The temperature dependence of ν_e is shown in Fig. S2. The fitting yields an activation energy $E_{a,\nu_e} = 0.44$ eV in reasonable agreement with $E_{a,\nu_e} = 0.56$ eV reported by Deb *et al.*[8]

n_0 turns out to be temperature independent in the range 55-75 °C. Thus the activation energy of the electron mobility, ν_e, shown in Fig. S2 is equal to that of $\sigma_e = q\nu_e n_0$, $E_{a,\sigma_e} = E_{a,\nu_e} = 0.44$ eV. This activation energy for σ_e is a typical polaron activation energy (0.5 eV) [3,10] and close to the experimental value reported for MoO_3, 0.43 eV.[11] The constant value of n_0 is plausible as the electrons originate from ionized oxygen vacancies the concentration of which is determined by the oxygen partial pressure during preparation. The vacancy hardly changes during the measurements due to the high electrode impedance for oxygen exchange.

The ratio $\alpha = \nu_e/\nu_i$ is determined by best fit. The positions of the peaks in Fig. S1 are sensitive to α. The temperature dependence of α is shown in Fig. S3. The activation energy is $E_{a,\alpha} = -0.47$ eV. From ν_e and α one determines the ion mobility, ν_i, which is presented in Fig. S4. The ion mobility activation energy is: $E_{a,\nu_i} = 0.91$ eV, about twice that of the electron mobility.

References

1   D. Kalaev and I. Riess, *Solid State Ionics*, 2013, **241**, 17–24.

2   D. Kalaev and I. Riess, *Solid State Ionics*, 2014, **262**, 883–888.

3   I. K. Naik and T. Y. Tien, *J. Phys. Chem. Solids*, 1978, **39**, 311–315.

4   D. Kalaev and I. Riess, *Solid State Ionics*, 2012, **212**, 26–42.

5   I. Riess, D. Kalaev and J. Maier, *Solid State Ionics*, 2013, **251**, 2–8.

6   I. Riess, M. Gödickemeier and L. J. Gauckler, *Solid State Ionics*, 1996, **90**, 91–104.

7   D. Kalaev, *Solid State Ionics*, 2014, **268**, 7–14.

8   S. K. Deb and J. A. Chopoorian, *J. Appl. Phys.*, 1966, **37**, 4818–4825.

9   Y. Aoki, C. Wiemann, V. Feyer, H.-S. Kim, C. M. Schneider, H. Ill-Yoo and M. Martin, *Nat. Commun.*, 2014, **5**, 3473.

10   H. Ding, H. Lin, B. Sadigh, F. Zhou, V. Ozoliņs and M. Asta, *J. Phys. Chem. C*, 2014, **118**, 15565–15572.

11   S. Berthumeyrie, J. C. Badot, J. P. Pereira-Ramos, O. Dubrunfaut, S. Bach and P. H. Vermaut, *J. Phys. Chem. C*, 2010, **114**, 19803–19814.
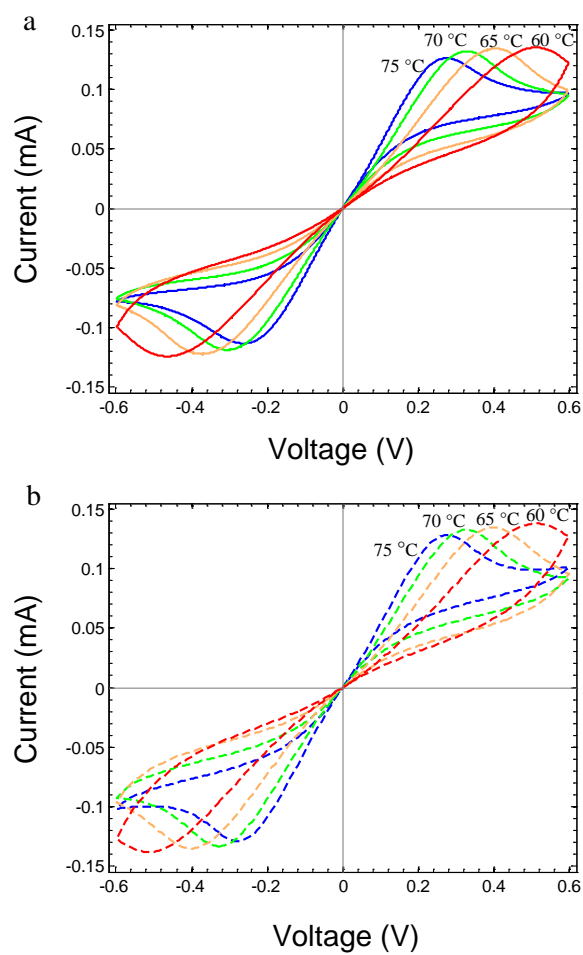
Fig. S1. (a) Measured and (b) fitted *I-V* relations at T = 60-75 °C for Au/MoO$_{3-\delta}$/Au device B,.

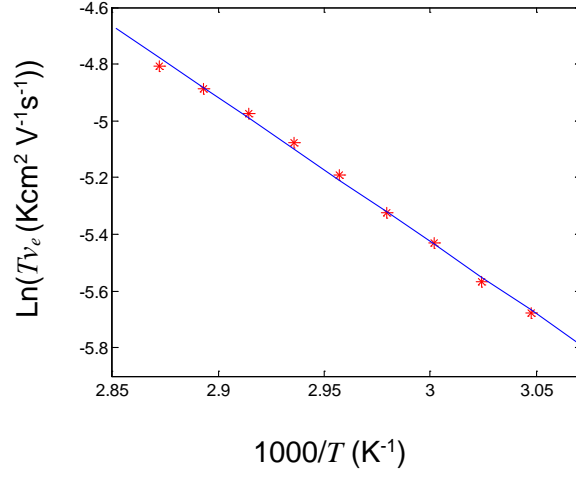Voltage sweep rate is 5×10^{-4} V/s at all temperatures.

Fig. S2. Red stars: electron mobility, v_e, of device B vs. reciprocal temperature in the range: $55 \leq T \leq 75$ °C. Solid blue line: fitted expression, $T v_{\mathrm{e}} = C \exp\left(-E_{a,\mathrm{e}}/(k_{\mathrm{B}}T)\right)$, $E_{\mathrm{a},v_{\mathrm{e}}} = 0.44$ eV C=const.
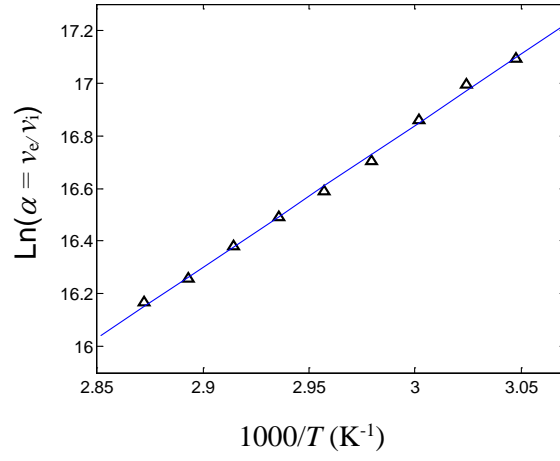
Fig. S3. Black triangles: $\alpha = \nu_e/\nu_i$ vs. reciprocal temperature, $55 \leq T \leq 75\ ^\circ C$, for device B. Blue

solid line: fitted expression, $\alpha = C\exp\left(-E_{a,\alpha}/\left(k_B T\right)\right)$, with $E_{a,\alpha} = -0.47$ eV, $C = $ Const.
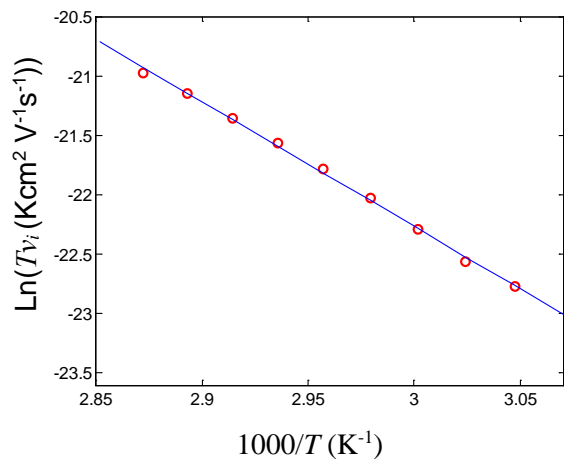
Fig. S4. Red circles: ion mobility vs. reciprocal temperature for device B. Blue solid line: fitted

expression, $T\nu_i = C\exp\left(-E_{a,\nu_i}/(k_B T)\right)$, $E_{a,\nu_i} = 0.91$, C = Const.