Electronic Supplementary Information for

Elastic resistance change and action potential generation of non-faradaic Pt/TiO₂/Pt capacitors

Hyungkwang Lim,^{*a,c*} Ho-Won Jang,^{*a*} Doh-Kwon Lee,^{*b*} Inho Kim,^{*a*} Cheol Seong Hwang,^{*c*} and Doo Seok Jeong*^{*a*}

^a Electronic Materials Research Centre, Korea Institute of Science and Technology, Hwarangno 14-gil
5, Seongbuk-gu, Seoul 136-791, Republic of Korea.

^b Solar Cell Research Centre, Korea Institute of Science and Technology, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea.

^c Department of Materials Science and Engineering, and Inter-university Semiconductor Research Centre, School of Engineering, Seoul National University, Seoul 151-744, Republic of Korea

*dsjeong@kist.re.kr

SI1. Counterclockwise hysteresis behaviour of a Pt/TiO₂/Pt non-faradaic capacitor

The counterclockwise (CCW) hysteresis in the high voltage region, shown in Fig. 1, was found to disappear at low voltage sweep rates. The ratio of a current density at a particular voltage during a downward sweep (J_{down}) to that of the same voltage during an upward sweep (J_{up}) was taken as a parameter representing the CCW hysteresis. Ratios larger than unity, therefore, indicate CCW hysteresis. As shown in Fig. SI1, at a voltage sweep rate of 0.001 V/s, the CCW hysteresis fades away within the first three J-V cycles. Increasing the voltage sweep rate makes the CCW hysteresis remain for more cycles, as in the 0.01 and 0.1 V/s cases, as shown in Fig. SI1. For the three rates, 0.1, 0.01, and 0.001 V/s, the time intervals between the current measurements at 1.5 V during the upward and

downward sweeps are 10, 100, and 1000 s, respectively. Thus, one may estimate the CCW hysteresis to retain itself for at least 100 s, since the CCW hysteresis at 0.01 V/s still somehow exists. However, it should be kept in mind that this CCW hysteresis occurs under high polarization conditions, i.e. polarization still prevails over depolarization. Therefore, under strong depolarization conditions, e.g. at zero voltage, higher current states as a result of the CCW hysteresis cannot be maintained for an extended period of time, i.e. the time constant of depolarization is small.



Figure SI1. Change of the CCW hysteresis in the high voltage region with respect to J-V cycle number at different voltage sweep rates.

SI2. Calculation of ionic current in a non-faradaic capacitor

In a mixed ionic-electronic conductor (MIEC), both electrons and mobile ions/defects contribute to the dc current. In a non-faradaic capacitor, the interface between the MIEC and electrode forms a blocking contact for mobile ions/defects. Hence, the number of the mobile ions/defects is conserved in the capacitor, i.e. they are confined in the MIEC. However, for electrons this capacitor is regarded as an open system connected to an electron reservoir. The dc ionic and electronic currents are described separately below.

Dc current in a MIEC is driven by two driving forces, chemical and galvani potential gradients. The former and the latter are termed diffusion and drift currents. Within the scope of a first-order approximation, the summation of drift and diffusion fluxes of charged particle *i*, j_{drift}^{i} and j_{diff}^{i} , through a one-dimensional electrode/MIEC/electrode capacitor, which is termed as drift-diffusion flux j_{dd}^{i} , is given by

$$j_{dd}^{i} = z_i c^i \mu_i E - D_i \frac{dc^i}{dx},\tag{S11}$$

where z_i , c^i , μ_i , D_i , and *E* denote the ionization number, the concentration, the mobility of particle *i*, the diffusion coefficient, and the internal electric field, respectively. The first and the second term on the right side of Eq. (SI1) mean the drift and the diffusion fluxes, respectively. Therefore, the dc ionic current density attributed to the drift-diffusion of particle *i* is $j_{dc}^i = z_i q j_{dd}^i$, where *q* means the elementary charge. For TiO₂ MIEC, $i = V_0^{\circ}$, denoting oxygen vacancy in the Kröger-Vink nomenclature.¹



Figure SI2. (a) Schematic of a non-faradaic capacitor utilizing an MIEC. A voltage is applied to the right electrode while the left electrode is grounded. (b) Configuration of the nodes in a one-dimensional non-faradaic capacitor in distance x and time t dimensions.

In a non-faradaic capacitor, the migration mobile ions/defects are confined within the MIEC, i.e. the drift-diffusion fluxes at the two interfaces of the capacitor are zero. That is, no exchange of ions/defects takes place through the interfaces. These boundary conditions play a key role in

evaluating the time-dependent distribution of ions/defects in the MIEC. When a faradaic-type capacitor is dealt with, appropriate formalism for ion/defect fluxes at the interface, e.g. the Butler-Volmer equation, can be used as boundary conditions instead.^{2, 3}

SI3. Calculation of dc electronic current in a non-faradaic capacitor

For electrons, the non-faradaic capacitor is not a closed system so that their injection into and ejection from the capacitor and their drift-diffusion in the MIEC should be taken into account. It was assumed here that electrons in the electrode exhibit free electronic behaviour and the MIEC has a single conduction band minimum. Also, it was assumed a mechanism for the injection of electrons from the electrode to the MIEC to be thermionic emission attributed to electron injection overcoming the band offset, i.e. Schottky barrier, at the electrode/MIEC interface.⁴ Electronic current density from the MIEC to electrode (reservoir), i.e. electron's flux from the electrode to the MIEC, is denoted by $j_{dc,1}^e$. The reverse current density $j_{dc,2}^e$, attributed to the electron's flux from the MIEC to the electrode, should also be considered to describe the dc electronic current density at the interface. This reverse current density can be expressed as the following equation:

$$j_{dc,2}^e = q v_r n_0, \tag{SI2}$$

where $v_r = \frac{A^*T^2}{qN_c}$, and A^* , *T*, and N_c denote the Richardson constant, temperature, the effect density of states for electrons in the MIEC.⁵ And n_0 in Eq. (SI2) indicates the concentration of electrons at the interface. In this model system, a voltage is applied to the right electrode as shown in Fig. SI2 a). In accordance, electric current along the positive x-axis is taken as positive. This results in the opposite polarity of electric current such as negative current under a positive voltage, however, later we make the polarity reversed. The net current density at the left interface in Fig. SI3 a) can therefore be written as $j_{dc}^e = j_{dc,1}^e - j_{dc,2}^e$, whereas that at the right interface $j_{dc}^e = -j_{dc,1}^e + j_{dc,2}^e$. These two equations serve as the boundary conditions for the electrons' transport through the capacitor.

Electronic current density in the MIEC is described in terms of the distribution of electrons and a gradient of their electrochemical potential, i.e. Fermi level ϵ_f . For a one-dimensional system, an electronic current density equation is $j_{dc}^e = n\mu_e d\epsilon_f/dx$, where *n* and μ_e denote electron concentration and electron's mobility, respectively. In addition, the electron concentration in the MIEC depends on the electron's effective mass m_e , the conduction band minimum ϵ_c , and the electron's electrochemical potential ϵ_f , through the following equation:

$$n = \int_{\epsilon_c}^{\infty} g(\epsilon) f(\epsilon) d\epsilon, \qquad (SI3)$$

where the density of states of electrons $g(\epsilon) = \frac{8\pi (2m_e^3)^{1/2}}{h^3} (\epsilon - \epsilon_f)^{1/2}$. Now, the electronic current density in the MIEC becomes a function of the distribution of the electrons' electrochemical potential and the galvani potential. Note that the conduction band minimum ϵ_c is a function of the galvani potential V through the equation, $\epsilon_c = \phi_b - qV$, where ϕ_b denotes the band offset at the electrode/MIEC interface.

The time-domain calculation of ionic and electronic current density cannot be performed using an analytical method, and thus the Crank-Nicolson method was employed, combing explicit and implicit finite difference methods.⁶ In this time-domain calculation, electrons' behaviour can be evaluated using a quasi-static approximation since electron's mobility is much larger compared to that of an ion or an ionic defect. Employing the quasi-static approximation gives the important condition that electronic current density is constant at all positions in the one-dimensional MIEC at a given time. This condition defines the relationship between galvani potential and electrochemical potential, implying that these two variables are dependent on each other. That is, if the distribution of galvani potential is known, so is that of electrochemical potential.

SI4. Calculation of time-dependent current in a non-faradaic capacitor

Considering the configuration of current density – voltage (J-V) measurements on a non-faradaic capacitor, a capacitor illustrated in Fig. SI2 a) together with an equivalent series resistance (ESR) should be taken into account. An ESR includes all possible resistance contributions in the configuration, e.g. electrode resistance, wire resistance, and internal resistance of the measurement setup. Concerning the voltage division in the configuration, an applied voltage V_{ap} , which is time-dependent, is expressed as

$$V_{ap} = -AR_{ESR}j + V_c, \tag{SI4}$$

where A, R_{ESR} , j, and V_c mean the area of the capacitor, the ESR, total current density including dc and displacement current, and the voltage drop along the capacitor, respectively. The total current density j is described as

$$j = j_{dc} - \epsilon_r \epsilon_0 \frac{d}{dt} \left(\frac{dV}{dx} \right), \tag{SI5}$$

where the first and the second terms on the right side of Eq. (SI5) denote dc and displacement currents, respectively. j_{dc} is the summation of dc ionic current j_{dc}^{i} and dc electronic current j_{dc}^{e} , which are discussed in Sections 1 and 2, respectively. ϵ_r , ϵ_0 , and V are a relative permittivity, the permittivity of vacuum, and galvani potential, respectively. Integrating Eq. (SI5) over time from zero to t'gives

$$\left. \frac{dV}{dx} \right|_{t=t'} = \left. \frac{dV}{dx} \right|_{t=0} + (\epsilon_r \epsilon_0)^{-1} \int_0^{t'} (j_{dc} - j) dt.$$
(SI6)

Again, by integrating Eq. (SI6) over x from zero to the capacitor thickness, $d_1 + d_2 + d_3$, one can evaluate the voltage assigned to the capacitor V_c at t' as follows:

$$V_c(t') = V_c(0) + \int_0^d (\epsilon_r \epsilon_0)^{-1} \int_0^{t'} (j_{dc} - j) dt dx.$$
(SI7)

Due to charge conservation, Fick's second law for electric charge in this one-dimensional capacitor is described as $dj_{dc}/dx = -d\rho/dt$, where ρ means charge density. Using the Poisson's equation, $\rho = dD/dx$, where D means dielectric displacement, $D = -\epsilon_r \epsilon_0 dV/dx$, Fick's second law can be rewritten as

$$\frac{d}{dx}\left(j_{dc} + \frac{dD}{dt}\right) = \frac{d}{dx}\left[j_{dc} - \epsilon_r \epsilon_0 \frac{d}{dt}\left(\frac{dV}{dx}\right)\right] = \frac{dj}{dx} = 0.$$
(S18)

Solutions of Eq. (SI8) are constant along axis x, meaning that the total current density j is not a function of x. Therefore, Eq. (SI7) can be rewritten as

$$V_{c}(t') = V_{c}(0) + \int_{0}^{d} (\epsilon_{r}\epsilon_{0})^{-1} \int_{0}^{t'} j_{dc} dt dx - \int_{0}^{d} (\epsilon_{r}\epsilon_{0})^{-1} dx \int_{0}^{t'} j dt.$$
 (SI9)

Entering Eq. (SI9) into Eq. (SI4) gives an equation relating an applied voltage V_{ap} to the dc current density j_{dc} and the total current density j as follows:

$$V_{ap} = -AR_{ESR}j + V_c(0) + \int_0^d (\epsilon_r \epsilon_0)^{-1} \int_0^{t'} j_{dc} dt dx - \int_0^d (\epsilon_r \epsilon_0)^{-1} dx \int_0^{t'} j dt.$$
(SI10)

For an easier calculation, Eq. (SI10) needs to be differentiated with respect to time, which leads to

$$\frac{dV_{ap}}{dt} = -AR_{ESR}\frac{dj}{dt} + \int_0^d (\epsilon_r \epsilon_0)^{-1} j_{dc} dx - j \int_0^d (\epsilon_r \epsilon_0)^{-1} dx.$$
(SI11)

Eq. (SI11) can be numerically solved using the Crank-Nicolson method.⁷ Nodes along x and t axes

are illustrated in Fig. SI2 b). Using the Crank-Nicolson method, Eq. (SI11) in the time interval $t_1 - (t_1 + \Delta t)$ is expressed as

$$\Delta t^{-1} \left[V_{ap}(t_1 + \Delta t) - V_{ap}(t_1) \right] = -AR_{ESR} \Delta t^{-1} \left[j(t_1 + \Delta t) - j(t_1) \right] + B_1 - B_2 j(t_1 + \Delta t),$$
(SI12)

where

$$B_1 = \sum_{i=1}^{n+1} (\epsilon_r \epsilon_0)^{-1} j_{dc}(t_1 + \Delta t) \Delta x, \tag{SI13}$$

and

$$B_2 = \epsilon_0^{-1} [\epsilon_{r1}^{-1} d_1 + \epsilon_{r2}^{-1} d_2 + \epsilon_{r3}^{-1} d_3].$$
(SI14)

where, $\epsilon_{r1}(d_1)$, $\epsilon_{r3}(d_3)$, and $\epsilon_{r2}(d_2)$ denote the relative permittivities (thicknesses) of the left Helmholtz layer, the right Helmholtz layer, and rest of the capacitor volume, respectively. Eq. (SI12) can be further rearranged by entering Eq. (SI4) into it as follows:

$$j(t_1 + \Delta t) = -(AR_{ESR} + B_2 \Delta t)^{-1} [V_{ap}(t_1 + \Delta t) - V_c(t_1) - B_1 \Delta t].$$
(SI15)

Insomuch as the current density j is constant in the MIEC at a given time, from Eq. (SI5), galvani potential distribution in the MIEC can be evaluated as far as the dc current j_{dc} in Eq. (SI5) is known at all position nodes in the MIEC at a given time.

As mentioned earlier, electron distribution in the MIEC can be simplified using the quasi-static approximation so that it is time-independent. However, ion/defect distribution should be taken into account in a time domain. Again, Fick's second law can be utilized for this purpose. Fick's second law for ion/defect i can therefore be described as

$$\frac{dc_i}{dt} = -\frac{dj_{dd}^i}{dx}.$$
(SI16)

The drift-diffusion flux of oxygen vacancies j_{dd}^i is a function of galvani potential and so is the concentration of ion/defect *i* via Eq. (SI16). For a non-faradaic capacitor based on TiO₂ MIEC, $i = V_0^{"}$ as mentioned earlier. In a non-faradaic capacitor, the drift-diffusion flux of oxygen vacancies j_{dd}^i is zero at the two interfaces so that this condition works as a boundary condition in solving Eq. (SI16).

As above-mentioned, all three different current types, j_{dc}^i , j_{dc}^e , and j, are given by functions of galvani potential distribution and they are indeed self-consistent equations. This means that, by means of an iteration method, one can evaluate the three quantities at all positions (nodes) in the MIEC as well as time nodes in a time domain. In this calculation, the Newton-Raphson iteration was utilized.

SI5. Impedance spectroscopy of a Pt/TiO₂/Pt non-faradaic capacitor

The dielectric constant of TiO_2 MIEC was determined from its admittance spectra. As suggested by Jeong et al., an equivalent circuit of a Pt/TiO₂/Pt capacitor is a parallel connection of a capacitor and a resistor.⁷ The admittance Yof this capacitor is

$$Y = j2\pi\omega C + 1/R,\tag{SI17}$$

where ω , *C*, and *R* denote frequency, the capacitance and the resistance of the capacitor, respectively. Therefore, from the imaginary part of an admittance spectrum, Im(Y), the capacitance can be extracted. For capacitors with five different pad-sizes, each Im(Y) spectrum is plotted in Fig. SI3 a). Note that, at frequencies below 1 MHz, neither open circuit nor short circuit calibration was necessary. The measured spectra show the good linearity of Im(Y) and frequency as shown in Fig. SI3 a). Eventually, the dielectric constant of TiO₂ is evaluated by plotting the capacitance vales of the five capacitors with respect to the pad-sizes. From the slope of the data in Fig. SI3 b), a dielectric constant of approximately 39 can be obtained. This value serves as one of critical parameters for the J-V calculations.



Figure SI3. (a) Admittance spectra (imaginary part) of Pt/TiO₂/Pt non-faradaic capacitors with five different pad-sizes. (b) Capacitance vales extracted from the admittance spectra with respect to pad-size. The dielectric constant of the MIEC was evaluated from the slope to be approximately 39.

SI6. Influence of oxygen gas injection during top electrode deposition on the CCW J-V hysteresis

To identify the nature of mobile point defects in a Pt/TiO₂/Pt capacitor, we fabricated a similar capacitor with injection oxygen gas during top electrode deposition. It can be predicted that top electrode deposition perhaps causes the reduction of TiO₂ MIEC in chemical and/or mechanical manners. To prevent this possible reduction, oxygen gas was injected while the Pt top electrode was deposited. For convenience, let us term this capacitor as Pt(O)/TiO₂/Pt. As can be seen in Fig. SI4, the oxygen injection process leads to significant shrinkage of CCW as well as CW J-V hysteresis. We estimate that the injected oxygen gas was used in the re-oxidation of the TiO₂ MIEC, and thus the number of oxygen vacancies is significantly reduced in the Pt(O)/TiO₂/Pt capacitor compared with a Pt/TiO₂/Pt capacitor. Therefore, this experimental result is believed to indicate oxygen vacancy as a type of the dominant point defect in the Pt/TiO₂/Pt capacitor.



Figure SI4. J-V hysteresis of a Pt(O)/TiO₂/Pt capacitor, compared with that of a Pt/TiO₂/Pt capacitor.

SI7. Conversion of an oxygen vacancy diffusion coefficient into an oxygen self-diffusion coefficient

The oxygen vacancy diffusion coefficient D_{V_0} used in the calculation is required to be converted into an oxygen self-diffusion coefficient D_0 for comparison with high-temperature oxygen self-diffusion coefficient data. This conversion can be done using the equation $D_0=c_{V_0}D_{V_0}/(c_0-c_{V_0})$, where c_0 and c_{V_0} denote oxygen ion and oxygen vacancy concentration, respectively. The oxygen ion concentration in our TiO₂ MIEC was assumed to be 6.4×10^{22} cm⁻³, which is that of single crystalline rutile TiO₂. The oxygen vacancy concentration in this calculation was 9×10^{18} cm⁻³, areal density of oxygen vacancies $(4.5 \times 10^{13} \text{ cm}^{-2})$ divided by the thickness of the TiO₂ film (d₂=50 nm). Thus, $c_0 >> c_{V_0}$, so that $D_0 \approx c_{V_0} D_{V_0}/c_0$, which is 7.03×10⁻¹⁷ cm²/s.

SI8. Dependence of the output current on input voltage pulse height and width

The output current of the non-faradaic capacitor was measured by applying voltage pulses of various heights and widths. An output current density map against the height and width of applied voltage pulses is plotted in Fig. SI5.



Figure SI5. Output current density map of the non-faradaic capacitor with respect to input voltage (V_{in}) height and width.

SI9. References

- 1. F. A. Kröger and H. J. Vink, *Solid State Phys.*, 1956, **3**, 307-435.
- 2. J. A. V. Butler, Trans. Faraday Soc., 1924, 19, 729.
- 3. T. Erdey-Gruz and M. Volmer, Z. Phys. Chem., 1930, 150, 203.
- 4. D. S. Jeong, H. Schroeder and R. Waser, *Phys. Rev. B*, 2009, **79**, 195317.
- 5. C. R. Crowell and M. Beguwala, *Solid-State Electron.*, 1971, 14, 1149-1157.
- K. W. Morton and D. F. Mayers, *Numerical Solution of Partial Differential Equations, An Introduction*, Cambridge University Press, Cambridge, 2005.
- 7. D. S. Jeong, H. Schroeder and R. Waser, *Appl. Phys. Lett.*, 2006, **89**, 082909.