Supplementary material

Electrochemical impedance spectroscopy (EIS) equivalent circuit fitting and extraction of electron transport parameters

The EIS spectra have been fitted by exploiting the equivalent circuit shown in Fig. S1, which includes contact resistance (R_S), equivalent impedance of the TiO_2 film, and a charge transfer impedance block (R_{CE} and Q_{CE}) [S1]. The mass transport impedance due to diffusion of electrolyte species has been neglected since it was not clearly visible in the measured frequency range (lowest measured frequency is 0.1 Hz).

According to a purely diffusive transport model of electrons across the TiO_2 film, the small-signal impedance of the TiO_2 film is modeled by the input impedance of the distributed RC circuit, open loaded, shown in Fig.S1 (bottom) [S2].

The constant phase elements Q_{CE} and Q_μ are a generalization of conventional capacitors, included to account for the possible frequency dispersion observed in the EIS spectra. The equivalent impedance of a generic constant phase element Q is given as

$$Z = \frac{1}{(i\omega)^\beta Q} \tag{1.1}$$

with $0 < \beta \le 1$, being $\beta = 1$ the case of the ideal capacitor.

The input impedance of the transmission line in Fig. S1 results as

$$Z_{\mathrm{TiO_2}} = \sqrt{\frac{R_{\mathrm{T}} R_{\mathrm{CT}}}{1+(i\omega/\omega_{\mathrm{CT}})^{\beta_{\mathrm{CT}}}}}\coth\left[\left(\frac{R_{\mathrm{T}}}{R_{\mathrm{CT}}}\right)^{\beta_{\mathrm{CT}}/2}\sqrt{1+(i\omega/\omega_{\mathrm{CT}})^{\beta_{\mathrm{CT}}}}\right] \tag{1.2}$$

with $\omega_{\mathrm{CT}} = (R_{\mathrm{CT}} Q_\mu)^{-1/\beta}$, while the overall impedance of the cell results as

$$Z = R_{\mathrm{S}} + Z_{\mathrm{TiO_2}} + R_{\mathrm{CE}} // Z_{\mathrm{CE}}, \tag{1.3}$$

being Z_{CE} the impedance of the constant phase element Q_{CE}. A few examples of Nyquist plots comparing the measured EIS spectra with the calculated ones are shown in Fig. S2-S4. The high frequency semicircles are ascribed to the charge transfer process at the electrolyte/Pt interface (R_{CE} and Z_{CE}) and to the transport of electrons across the TiO_2 film (R_T), while the larger semicircles in the low frequency range are associated to the recombination mechanisms in the TiO_2 film (R_{CT}, Q_μ).

Finally, from the fitting parameters $R_{\mathrm{T}}, R_{\mathrm{CT}}, \omega_{\mathrm{CT}}$, the effective electron lifetime τ_n and diffusion length L_n are evaluated as

$$L_n = d\sqrt{R_{\mathrm{CT}}/R_{\mathrm{T}}}\,,\ \tau_n = 1/\omega_{\mathrm{CT}}. \tag{1.4}$$

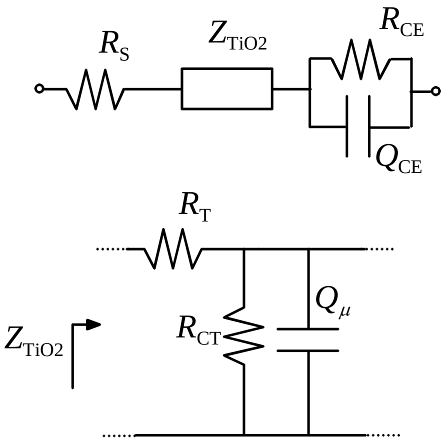

Figure S1. Equivalent circuit exploited for the fitting of the EIS spectra. Top: equivalent circuit of the overall cell; bottom: transmission line model of the TiO2 film

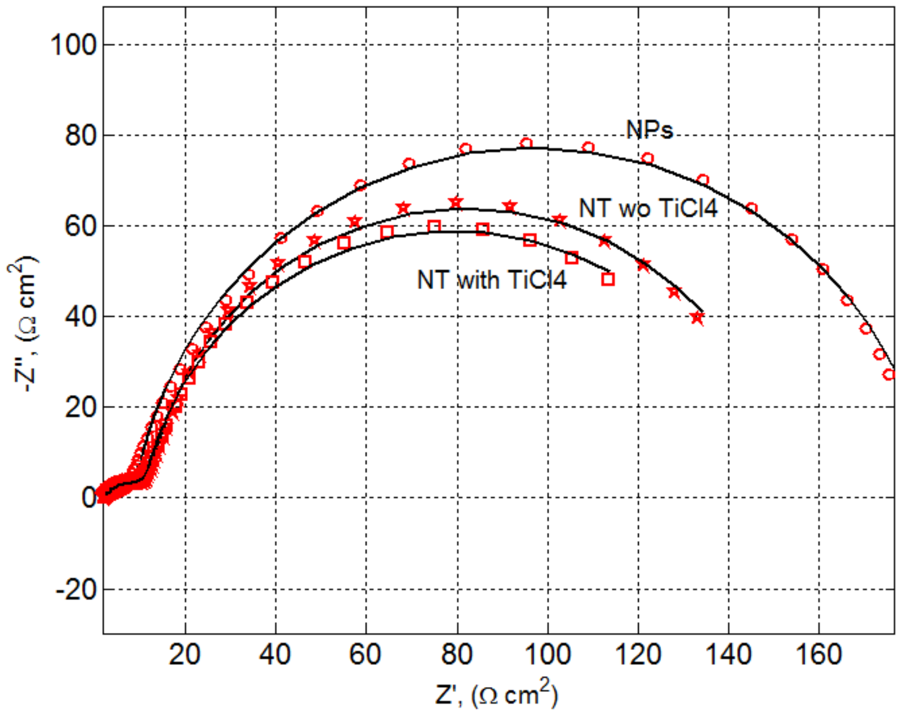

Figure S2. Measured (symbol) and fitted (solid line) EIS spectra at the lowest bias voltage

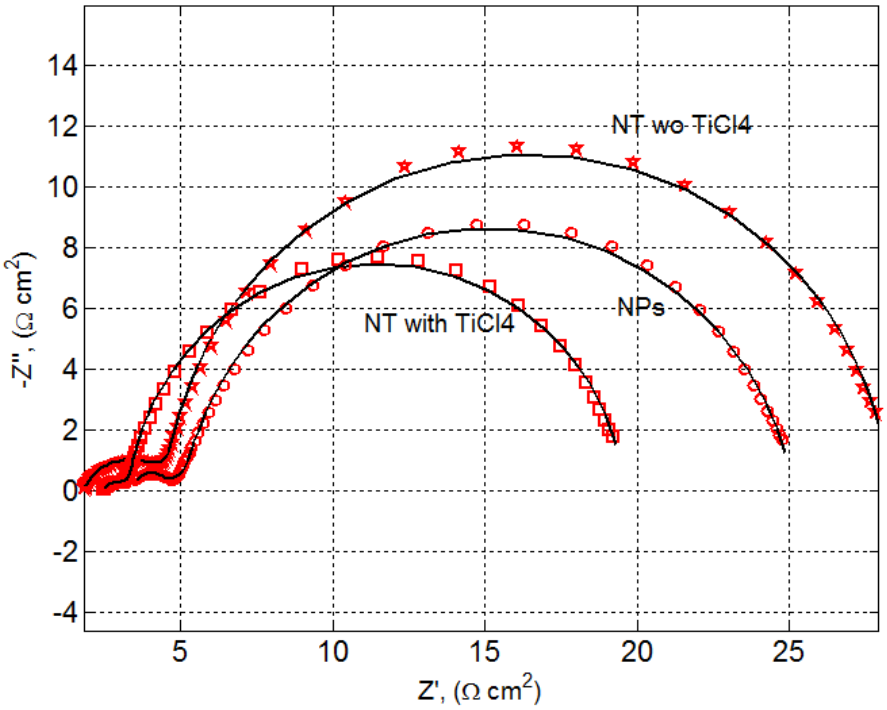

Figure S3. Measured (symbol) and fitted (solid line) EIS spectra at medium bias voltage

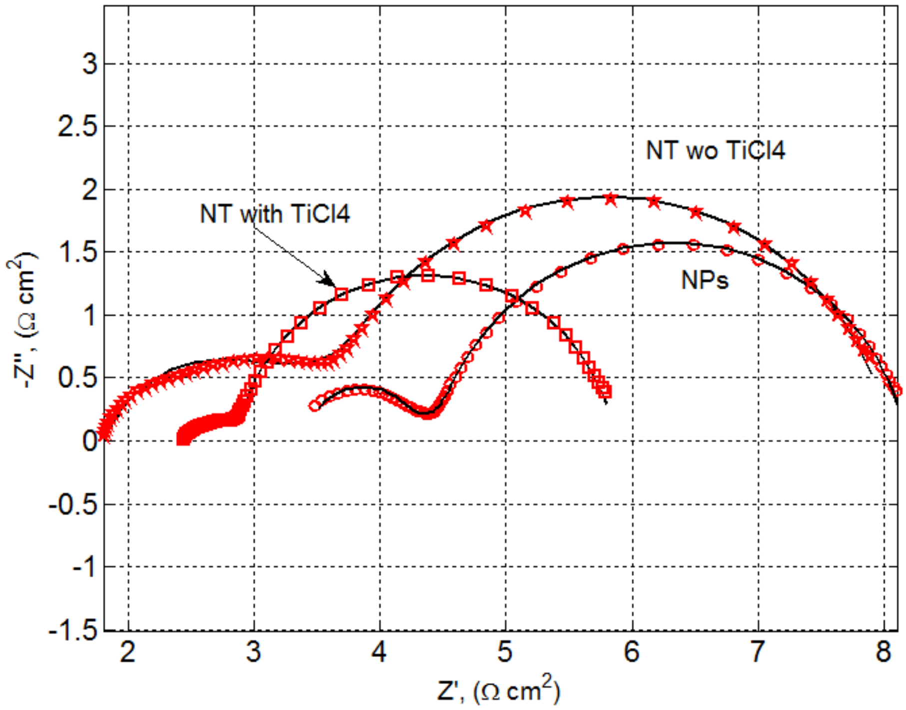

Figure S4. Measured (symbol) and fitted (solid line) EIS spectra at the highest bias voltage

References

[S1] J. Halme, P. Vahermaa, K. Miettunen and P. Lund, *Adv. Mater*, 2010, **22**, E210

[S2] J. Bisquert, G. Garcia-Belmonte, F. Fabregat-Santiago, N.S. Ferriols, P. Bogdanoff and E.C. Pereira, *J. Phys. Chem. B,* 2000, **104**, 2287