Evidencing Fast, Massive and Reversible H^+-Insertion in Nanostructured TiO_2 Electrodes at Neutral pH. Where Do Protons Come From?

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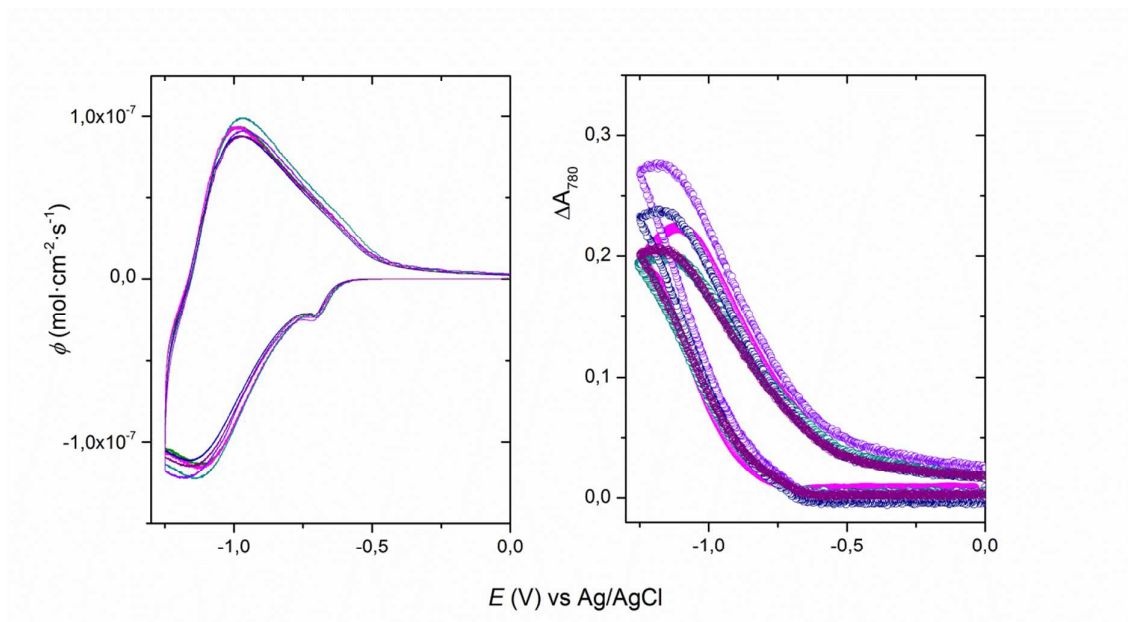Email: veronique.balland@univ-paris-diderot.fr
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Figure S1. (Left) CVs and (right) CVAs ($\lambda = 780$ nm) recorded at 7 different 1 μm-thick GLAD-TiO$_2$ electrodes (arising from 2 different GLAD deposition batches) in 0.1 M HEPES (pH 7.0) and 0.3 M KCl. Each color denotes a simultaneously recorded CV/CVA pair . Scan rate: 0.1 V·s^{-1}. $T = 25°C$.
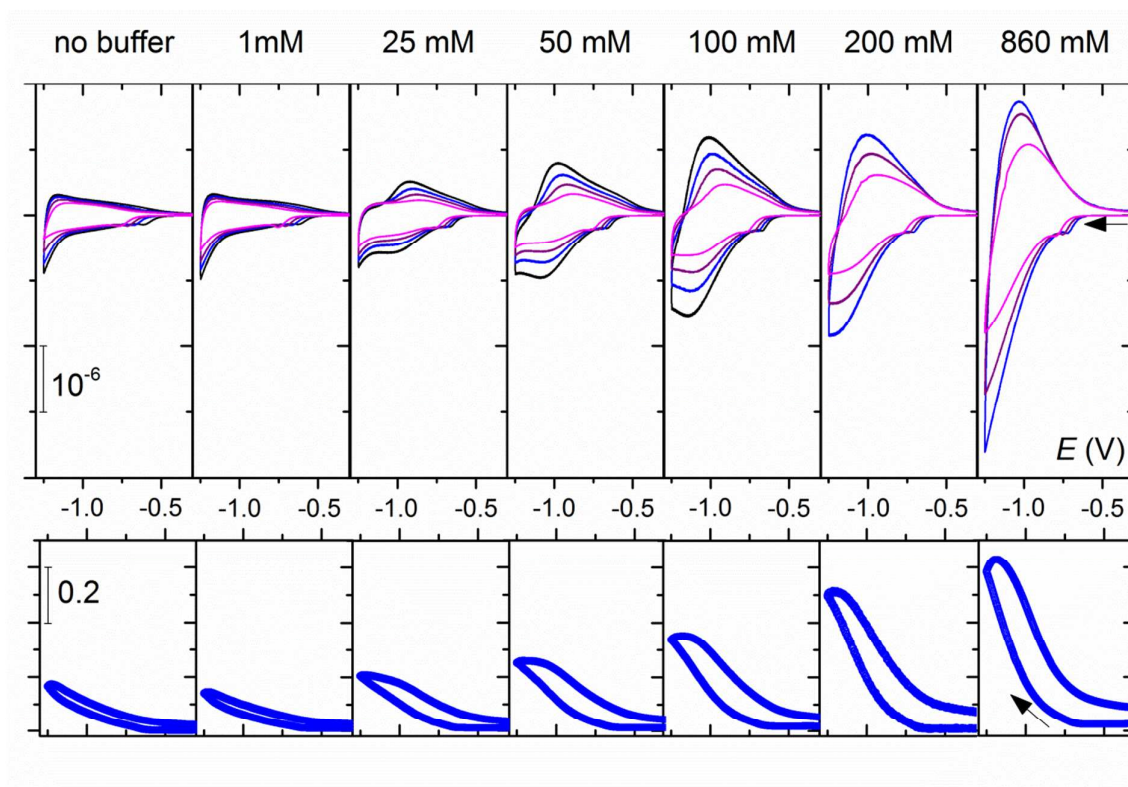
Figure S2. Top: CVs recorded at 1 μm-thick GLAD-TiO$_2$ electrodes in aqueous solutions of 0.3 M KCl complemented with increasing concentration of HEPES buffer (pH 7.0). Buffer concentrations C$_B$ are reported on top of the graphs, and currents are converted to electron flux density normalized to the scan rate. The ordinate is $\phi/v = i/FSv$ with units mol·V^{-1}·cm^{-2}. Scan rates: 0.05 V·s^{-1} (black), 0.1·V s^{-1} (blue), 0.2 V·s^{-1} (purple) and 0.5 V·s^{-1} (magenta). Bottom: CVAs ($\lambda = 780$ nm) recorded during the 0.1 V·s^{-1} CV scans. The ordinate is in absorbance units. The abscissa for both the CVs and CVAs are potential (V) with respect to the Ag/AgCl (3 M KCl) reference electrode. $T = 25$°C.
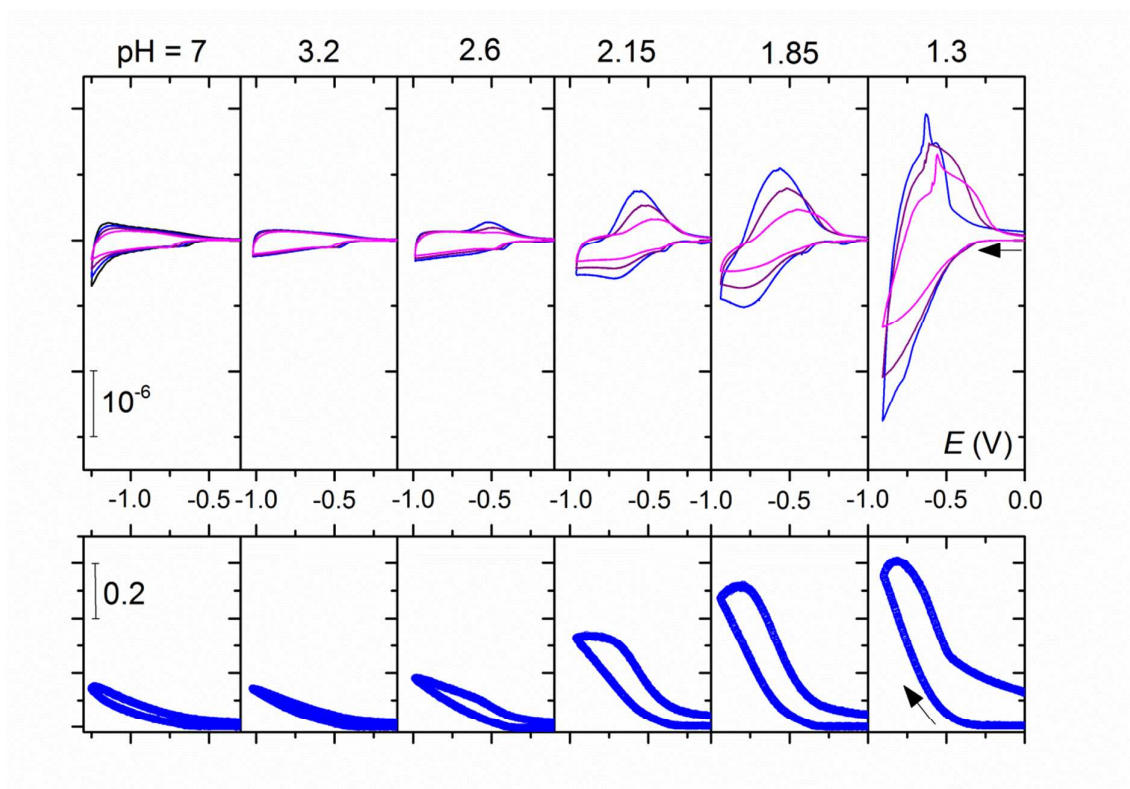
Figure S3. Top: CVs recorded at 1 μm-thick GLAD-TiO$_2$ electrodes immersed in increasingly acidic aqueous solutions (pHs are reported above the graphs). Currents are converted to electron flux density normalized to the scan rate. The ordinate is $\phi/v = i/FSv$ with units mol·V^{-1}·cm^{-2}. Scan rates: 0.05 V·s^{-1} (black), 0.1 V·s^{-1} (blue), 0.2 V·s^{-1} (purple) and 0.5 V·s^{-1} (magenta). Bottom: CVAs ($\lambda = 780$ nm) recorded simultaneously to the CVs (only experiments conducted at 0.1 V·s^{-1} are shown). The ordinate is in absorbance units. The abscissa for both the CVs and CVAs are potential (V) with respect to the Ag/AgCl (3 M KCl) reference electrode. $T = 25°C$.
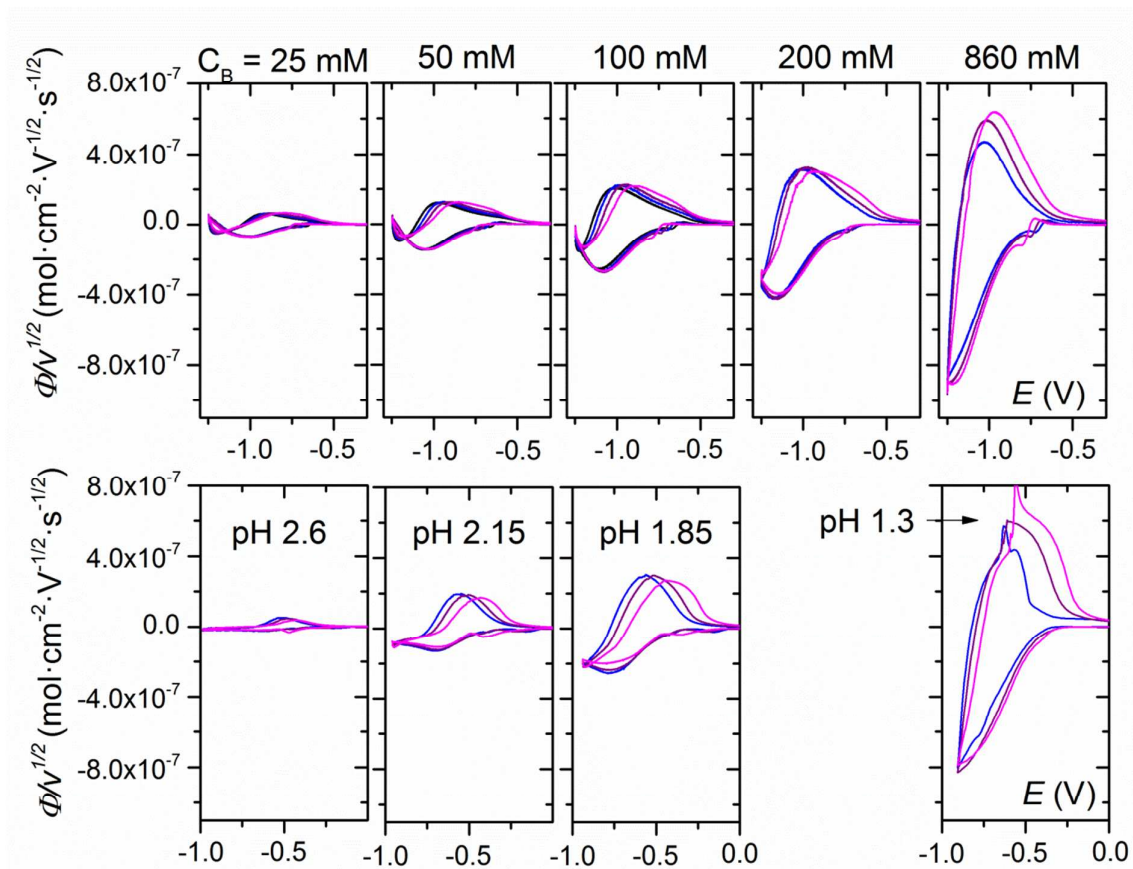
Figure S4. Top: CVs previously presented in Figure S2 with correction to remove the capacitive contribution to the total current (i.e., by subtracting the CVs recorded in 0.3 M KCl without buffer). Bottom: CVs previously presented in Figure S3 with correction to remove the capacitive contribution to the total current (i.e., by subtracting the CVs recorded in 0.3 M KCl). Currents were all converted to electron flux density normalized to the square root of scan rate. Scan rates: 0.05 V·s^{-1} (black), 0.1 V·s^{-1} (blue), 0.2 V·s^{-1} (purple) and 0.5 V·s^{-1} (magenta). The abscissa are potential (V) with respect to the Ag/AgCl (3 M KCl) reference electrode. $T = 25°C$.
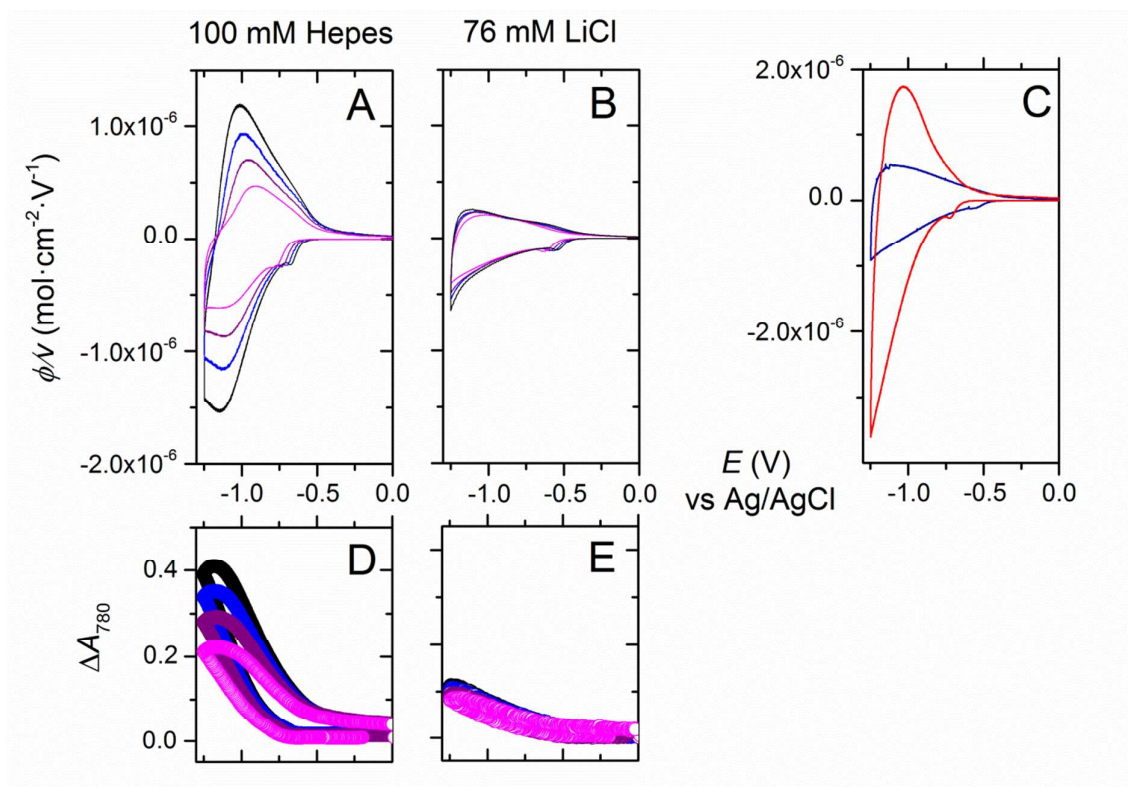
Figure S5. (A,B) CVs recorded at 1 μm-thick GLAD-TiO$_2$ electrodes immersed in aqueous solutions containing 0.3 M KCl and (A) 76 mM acidic form of HEPES (i.e. 0.1 M HEPES buffer, pH 7.0) and (B) 76 mM LiCl. Scan rates: 0.05 V·s^{-1} (black), 0.1 V·s^{-1} (blue), 0.2 V·s^{-1} (purple) and 0.5 V·s^{-1} (magenta). (C) Same as (A,B) but with 0.3 M KCl and (red) 0.66 M acidic form of HEPES (0.66 M AH in 0.86 M HEPES, pH 7.0) or (dark blue) 1 M LiCl, both recorded at a scan rate of 0.1 V·s^{-1}. (D,E) CVAs (λ = 780 nm) recorded during the corresponding CV scans in (A,B). T = 25°C.
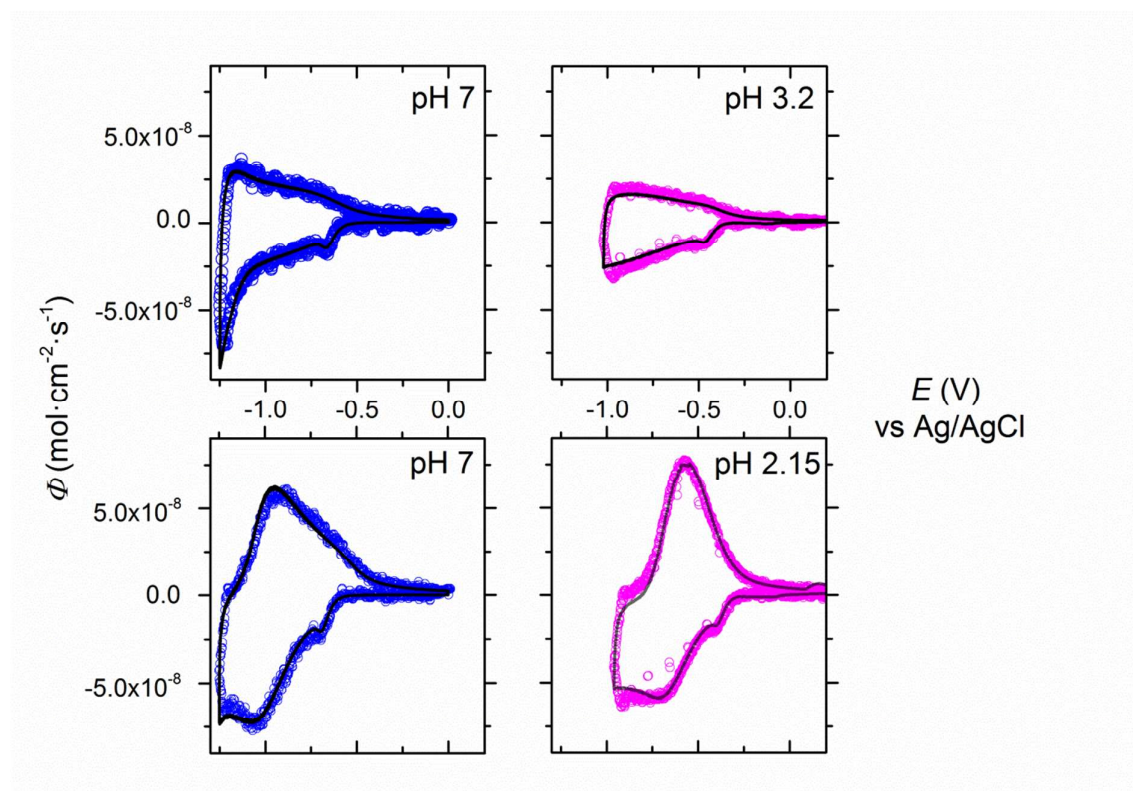
Figure S6. CVs (black line) and DCVAs (circles) expressed in flux density and recorded at (left) neutral pH in the presence of (top) 1 mM or (bottom) 50 mM HEPES, or (right) acidic pHs. The optimized overlay of DCVAs and CVs was obtained by adjusting the ε_{780} value to (blue) 800 $M^{-1} \cdot cm^{-1}$ and (magenta) 1200 $M^{-1} \cdot cm^{-1}$. All experiments were conducted in the presence of 0.3 M KCl at a scan rate of 0.1 $V \cdot s^{-1}$. $T = 25°C$.

Table S1. Features of CVs and CVAs shown in Figure 2.

pH	1.85	7	7
$[H_3O^+]$ (mM)	14	~0	~0
[AH] (mM)	-	0	77
E_{onset} (V)[a]	-0.30	-0.60	-0.60
$E^{0'}$ (V)[b]	-0.68	-	- 1.06
ΔE_p (mV)	220	-	120
$\Delta A_{780}{}^{max}$	0.51	0.15	0.34
ε_{780} (M^{-1} cm^{-1})	1200	800	800

[a] Potential that characterize the onset increase of absorbance measured at 780 nm.
[b] Formal potential obtained from the average of cathodic and anodic peak potentials at the slowest scan rate.