

Evidencing Fast, Massive and Reversible H⁺- Insertion in Nanostructured TiO₂ Electrodes at Neutral pH. Where Do Protons Come From?

Yee-Seul Kim,[†] Sébastien Kriegel,[†] Kenneth D. Harris,^{#,§} Cyrille Costentin,[†]

Benoît Limoges^{†,} and Véronique Balland^{†,*}*

[†] Laboratoire d'Electrochimie Moléculaire, UMR CNRS 7591, Université Paris Diderot,
Sorbonne Paris Cité, 15 rue Jean-Antoine de Baïf, F-75205 Paris Cedex 13, France

[#] NRC National Institute for Nanotechnology, Edmonton, Alberta, Canada T6G 2M9 and
Department of Mechanical Engineering, University of Alberta, Edmonton, Alberta, Canada
T6G 2V4 .

[§] Leibniz-Institute für Polymerforschung Dresden, 01069 Dresden, Germany

Email: veronique.balland@univ-paris-diderot.fr
limoges@univ-paris-diderot.fr

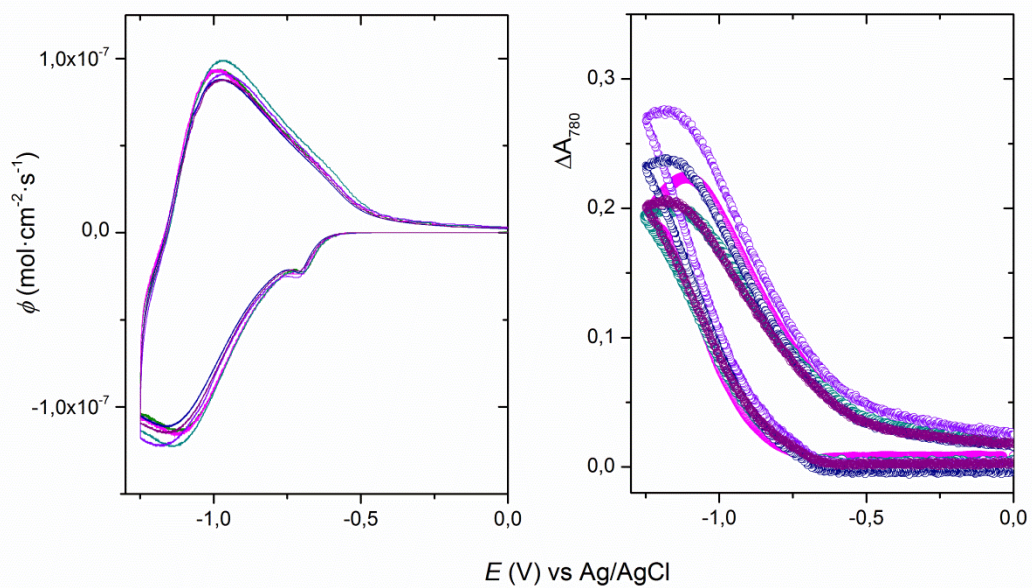


Figure S1. (Left) CVs and (right) CVAs ($\lambda = 780$ nm) recorded at 7 different 1 μm -thick GLAD-TiO₂ electrodes (arising from 2 different GLAD deposition batches) in 0.1 M HEPES (pH 7.0) and 0.3 M KCl. Each color denotes a simultaneously recorded CV/CVA pair . Scan rate: $0.1 \text{ V}\cdot\text{s}^{-1}$. $T = 25^\circ\text{C}$.

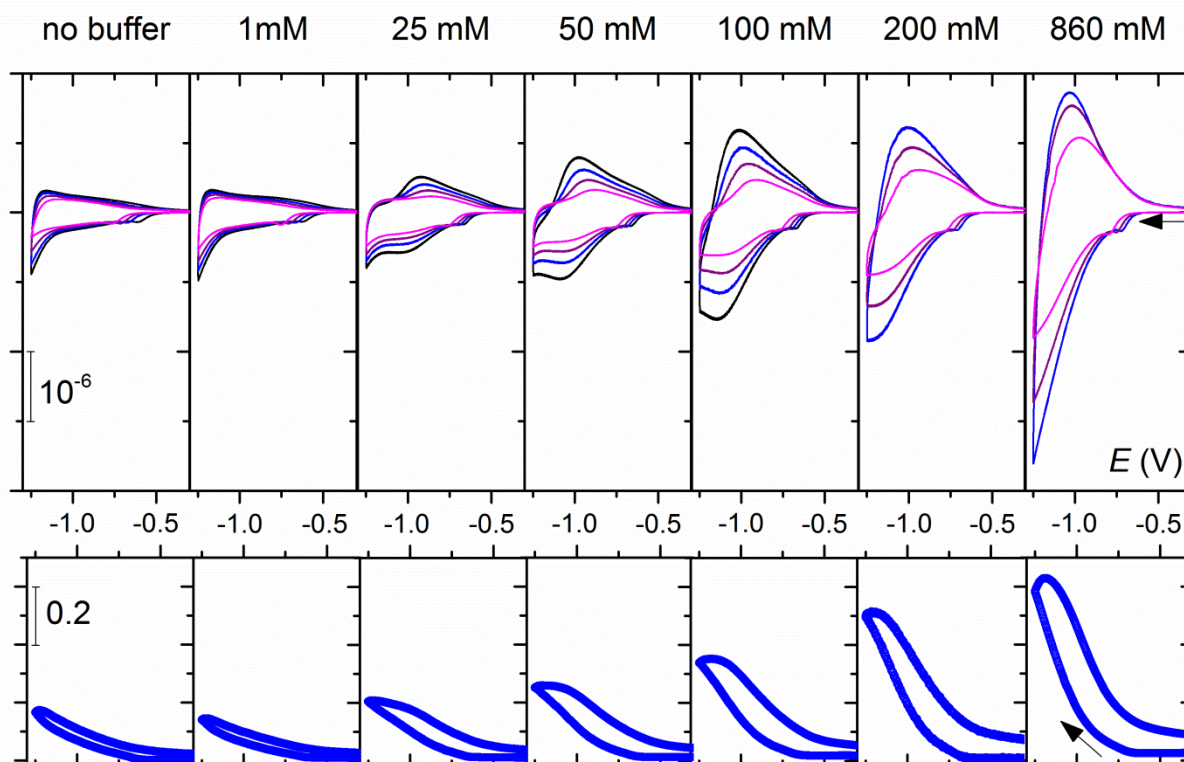


Figure S2. Top: CVs recorded at 1 μm -thick GLAD-TiO₂ electrodes in aqueous solutions of 0.3 M KCl complemented with increasing concentration of HEPES buffer (pH 7.0). Buffer concentrations C_B are reported on top of the graphs, and currents are converted to electron flux density normalized to the scan rate. The ordinate is $\phi/v = i/FSv$ with units $\text{mol}\cdot\text{V}^{-1}\cdot\text{cm}^{-2}$. Scan rates: $0.05\text{ V}\cdot\text{s}^{-1}$ (black), $0.1\text{ V}\cdot\text{s}^{-1}$ (blue), $0.2\text{ V}\cdot\text{s}^{-1}$ (purple) and $0.5\text{ V}\cdot\text{s}^{-1}$ (magenta). Bottom: CVAs ($\lambda = 780\text{ nm}$) recorded during the $0.1\text{ V}\cdot\text{s}^{-1}$ 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. $T = 25^\circ\text{C}$.

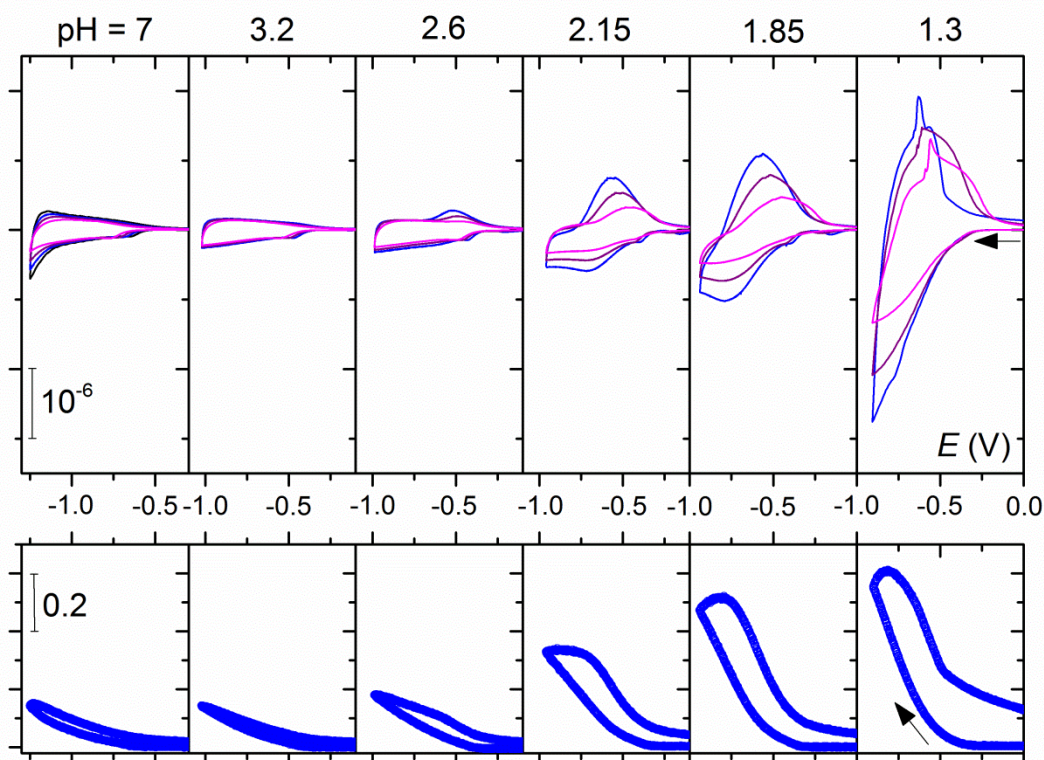


Figure S3. Top: CVs recorded at 1 μm -thick GLAD- TiO_2 electrodes immersed in increasingly acidic aqueous solutions (pHs are reported above the graphs). Currents are converted to electron flux density normalized to the scan rate. The ordinate is $\phi/v = i/FSv$ with units $\text{mol}\cdot\text{V}^{-1}\cdot\text{cm}^{-2}$. Scan rates: 0.05 $\text{V}\cdot\text{s}^{-1}$ (black), 0.1 $\text{V}\cdot\text{s}^{-1}$ (blue), 0.2 $\text{V}\cdot\text{s}^{-1}$ (purple) and 0.5 $\text{V}\cdot\text{s}^{-1}$ (magenta). Bottom: CVAs ($\lambda = 780$ nm) recorded simultaneously to the CVs (only experiments conducted at 0.1 $\text{V}\cdot\text{s}^{-1}$ 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. $T = 25^\circ\text{C}$.

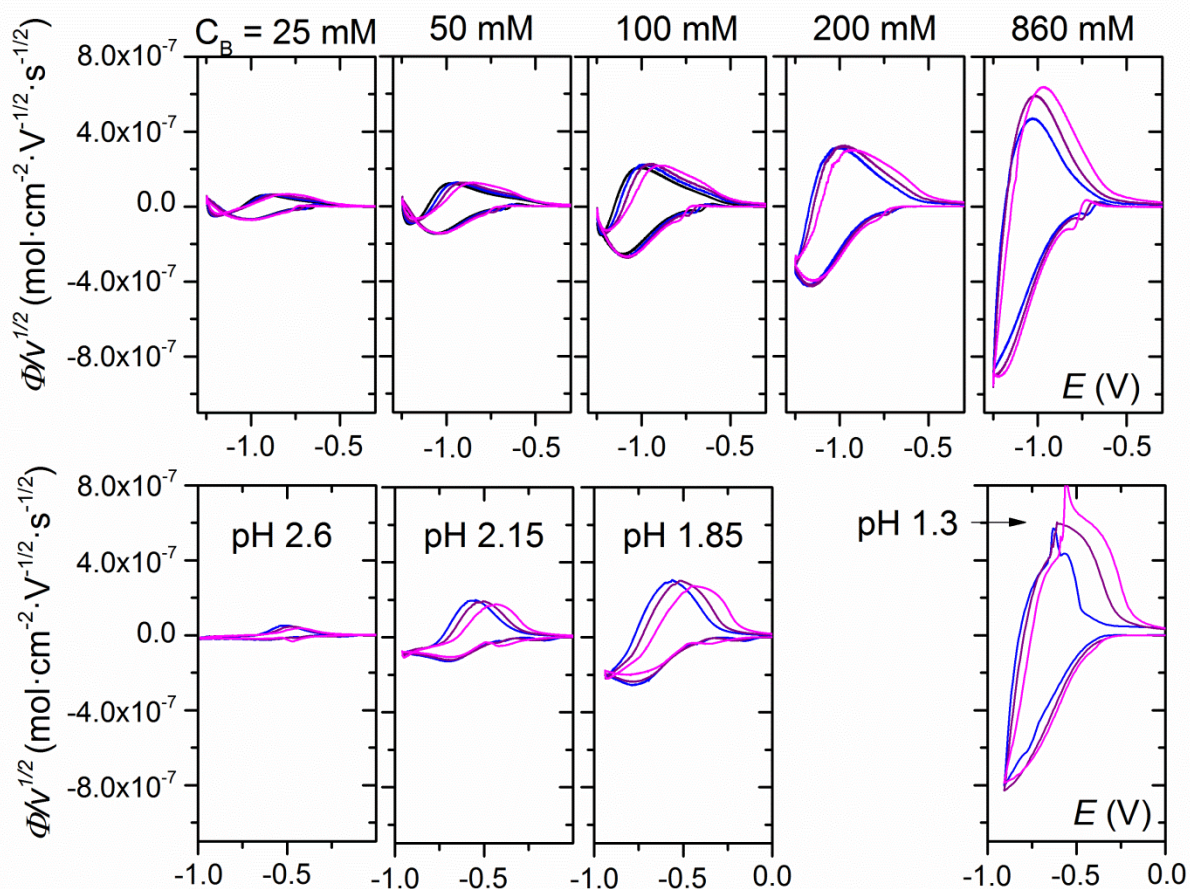


Figure S4. Top: CVs previously presented in Figure S2 with correction to remove the capacitive contribution to the total current (i.e., by subtracting the CVs recorded in 0.3 M KCl without buffer). Bottom: CVs previously presented in Figure S3 with correction to remove the capacitive contribution to 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: $0.05 \text{ V}\cdot\text{s}^{-1}$ (black), $0.1 \text{ V}\cdot\text{s}^{-1}$ (blue), $0.2 \text{ V}\cdot\text{s}^{-1}$ (purple) and $0.5 \text{ V}\cdot\text{s}^{-1}$ (magenta). The abscissa are potential (V) with respect to the Ag/AgCl (3 M KCl) reference electrode. $T = 25^\circ\text{C}$.

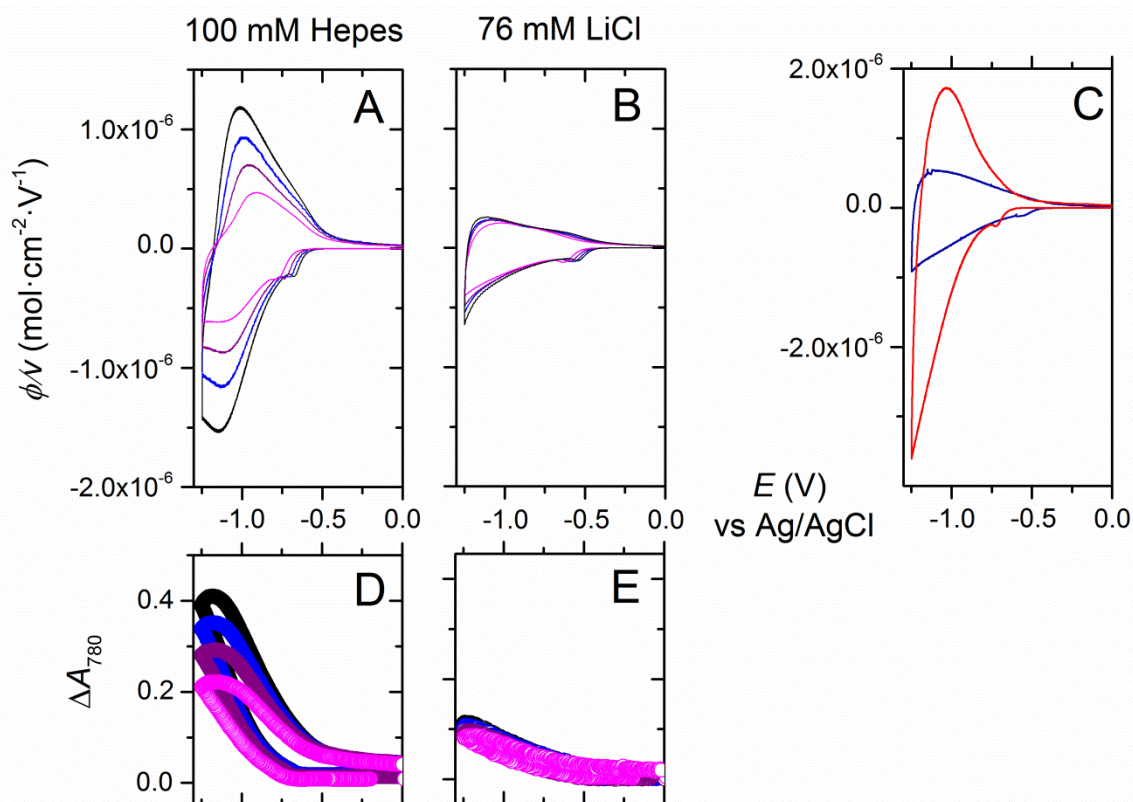


Figure S5. (A,B) CVs recorded at 1 μm -thick GLAD-TiO₂ electrodes immersed in aqueous solutions containing 0.3 M KCl and (A) 76 mM acidic form of HEPES (i.e. 0.1 M HEPES buffer, pH 7.0) and (B) 76 mM LiCl. Scan rates: 0.05 V·s⁻¹ (black), 0.1 V·s⁻¹ (blue), 0.2 V·s⁻¹ (purple) and 0.5 V·s⁻¹ (magenta). (C) 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 ($\lambda = 780$ nm) recorded during the corresponding CV scans in (A,B). $T = 25^\circ\text{C}$.

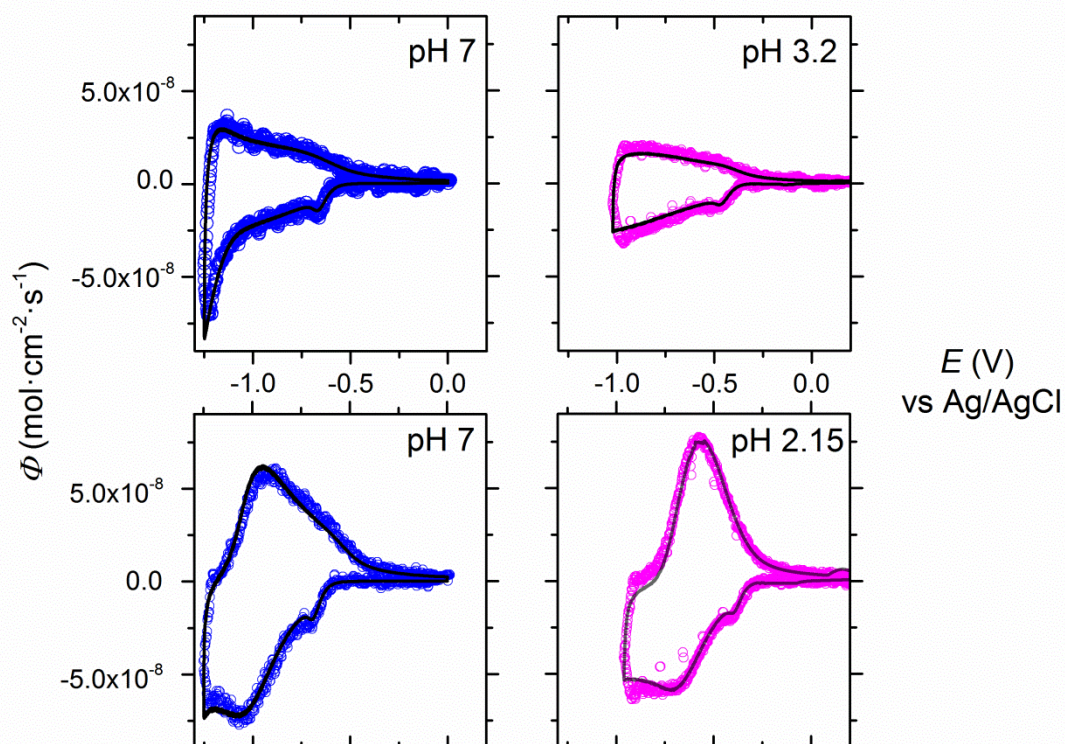


Figure S6. CVs (black line) and DCVAs (circles) expressed in flux density and recorded at (left) neutral pH in the presence of (top) 1 mM or (bottom) 50 mM HEPES, or (right) acidic pHs. The optimized overlay of DCVAs and CVs was obtained by adjusting the ϵ_{780} value to (blue) $800 \text{ M}^{-1}\cdot\text{cm}^{-1}$ and (magenta) $1200 \text{ M}^{-1}\cdot\text{cm}^{-1}$. All experiments were conducted in the presence of 0.3 M KCl at a scan rate of $0.1 \text{ V}\cdot\text{s}^{-1}$. $T = 25^\circ\text{C}$.

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
ΔA_{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.