Supplemental information

Mechanism of chloride inhibition of bilirubin oxidases and its dependence on potential and pH.

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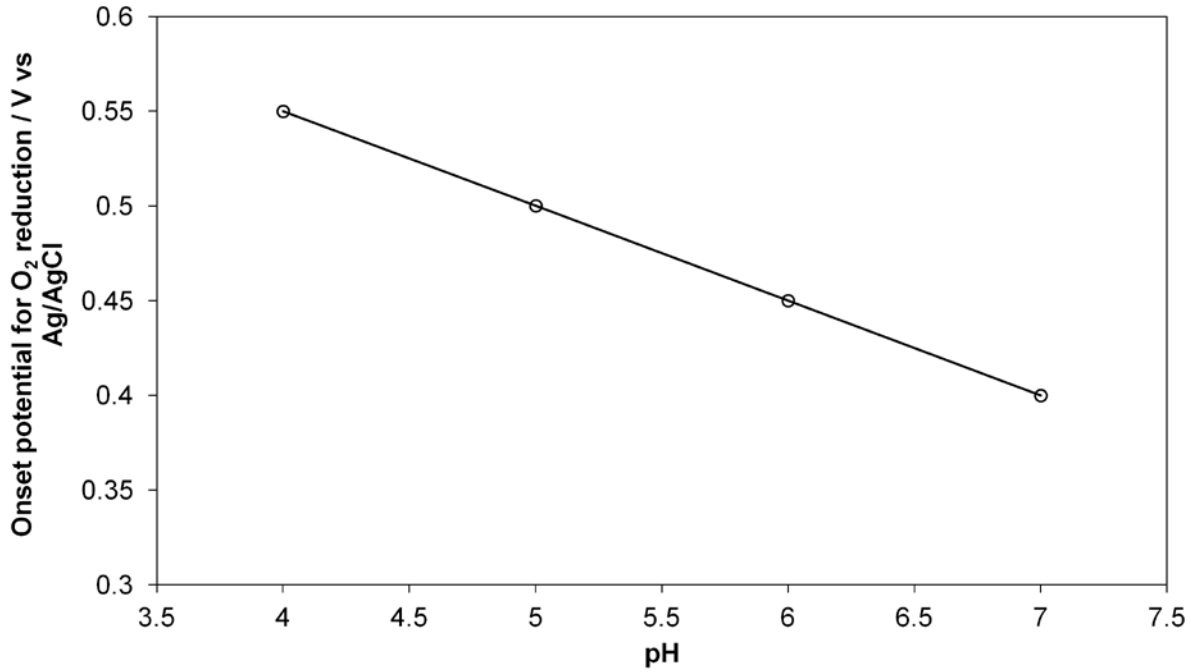


Figure SI1. Dependence of onset for O_2 reduction on pH for *B. pumilus* BOD adsorbed at a CNF-modified pyrolytic graphite electrode in O_2 saturated 200-100 mM phosphate-citrate buffer at T = 50°C.

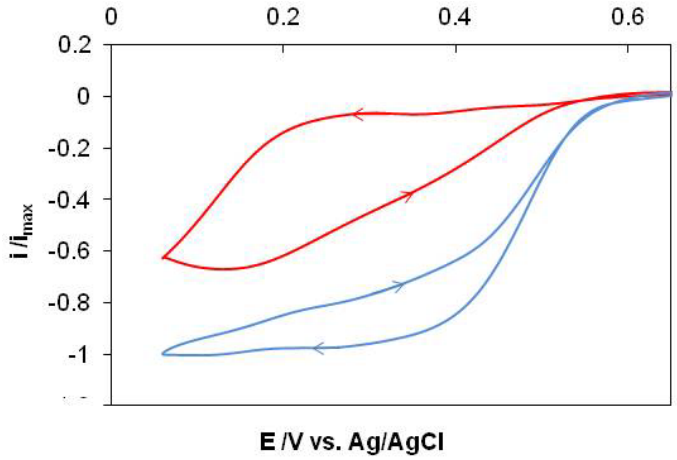


Figure SI2. CV of *B. pumilus* BOD adsorbed at a bare pyrolytic graphite electrode before (blue curve) and after 15 mM NaCl addition (red curve) in O_2 saturated 200-100 mM phosphate-citrate buffer pH 4 at T = 50°C. Scan rate: 5 $mV.s^{-1}$.

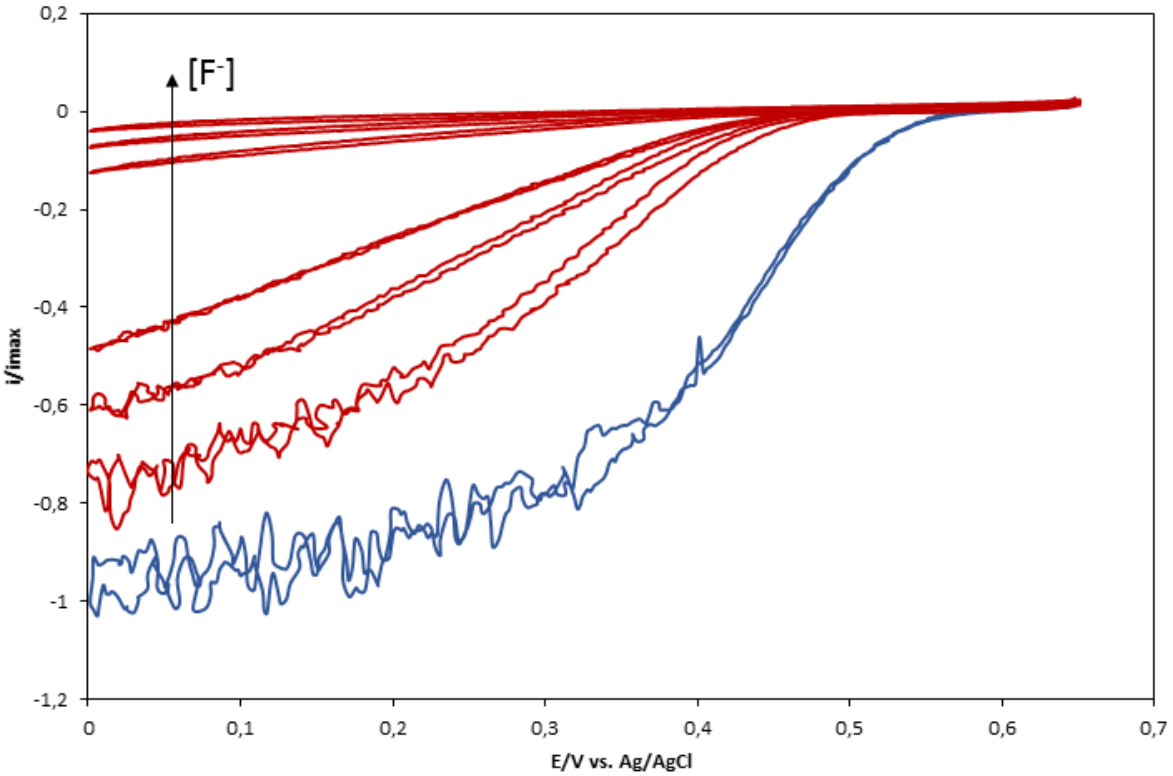


Figure SI3. CVs of *B. pumilus* BOD adsorbed at a CNF-modified pyrolytic graphite electrode before (blue curve) and after NaF addition (red curves). The arrow shows the increase of NaF concentrations (respectively 10, 20, 30, 40, 50 and 80 mM). O_2 saturated 200-100 mM phosphate-citrate buffer pH 4 at T = 37°C. Scan rate: 5 $mV.s^{-1}$.

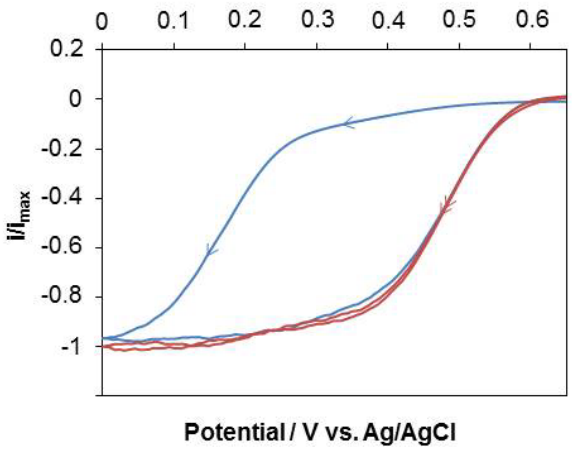


Figure SI4. *B. pumilus* BOD reactivation after NaCl removal from the electrolyte. CV curves at 5 $mV.s^{-1}$ in O_2 saturated 200-100 mM phosphate-citrate buffer pH 4 at T = 50°C, first scan (blue curve) and second scan (red curve).

		Relative Enzyme Activity (%)		
Ligand-Buffer pH	**[NaCl]**	**0 mM**	**100 mM**	**200 mM**
ABTS - pH4		100 ± 7.4	2.4 ± 2	0,6 ± 0.6
ABTS - pH5		100 ± 13.1	54.3 ± 24	28 ± 10.2
ABTS - pH6		100 ± 3.9	95.3 ± 8.2	87.8 ± 2.4
ABTS - pH7		100 ± 4.2	91.2 ± 13.5	87.5 ± 1
SGZ - pH7		100 ± 4.2	96 ± 3.3	92.3 ± 3.1

Table SI1. Residual enzyme activity measured either with ABTS or SGZ by *B. pumilus* BOD after 10 minutes incubation in 100 or 200 mM NaCl as a function of pH. Phosphate-citrate buffer 200-100 mM, T = 37°C.

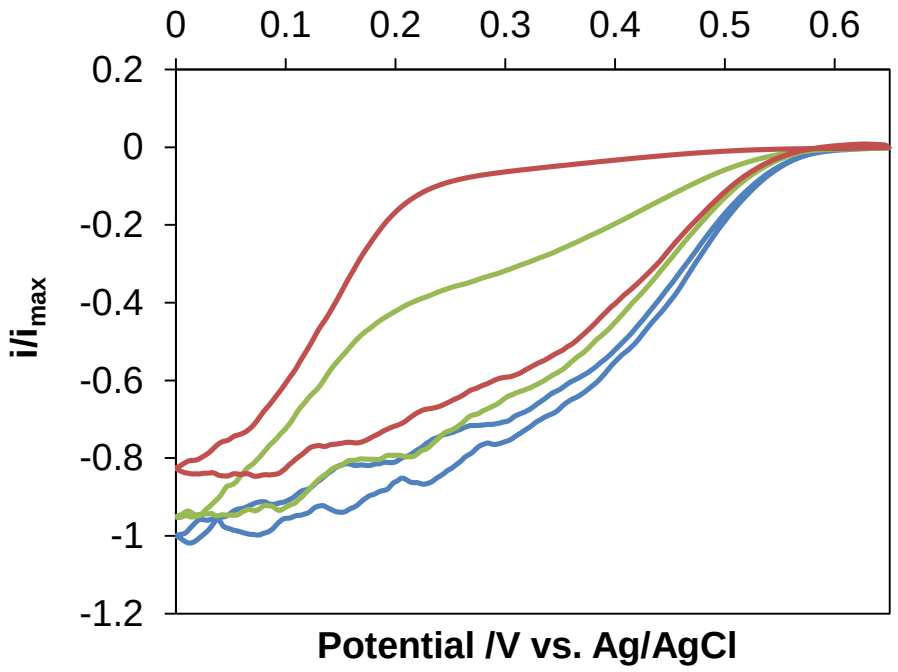


Figure SI5: O_2 reduction by *B. pumilus* BOD at pH 4 and 37°C: CV curves at 5 $mV.s^{-1}$ in 200-100 mM phosphate-citrate buffer. Increasing incubation times in 5 mM NaCl: 0 min (blue curve); 15 min (green curve) and 30 min (red curve). Electrodes modified as in Fig 1.

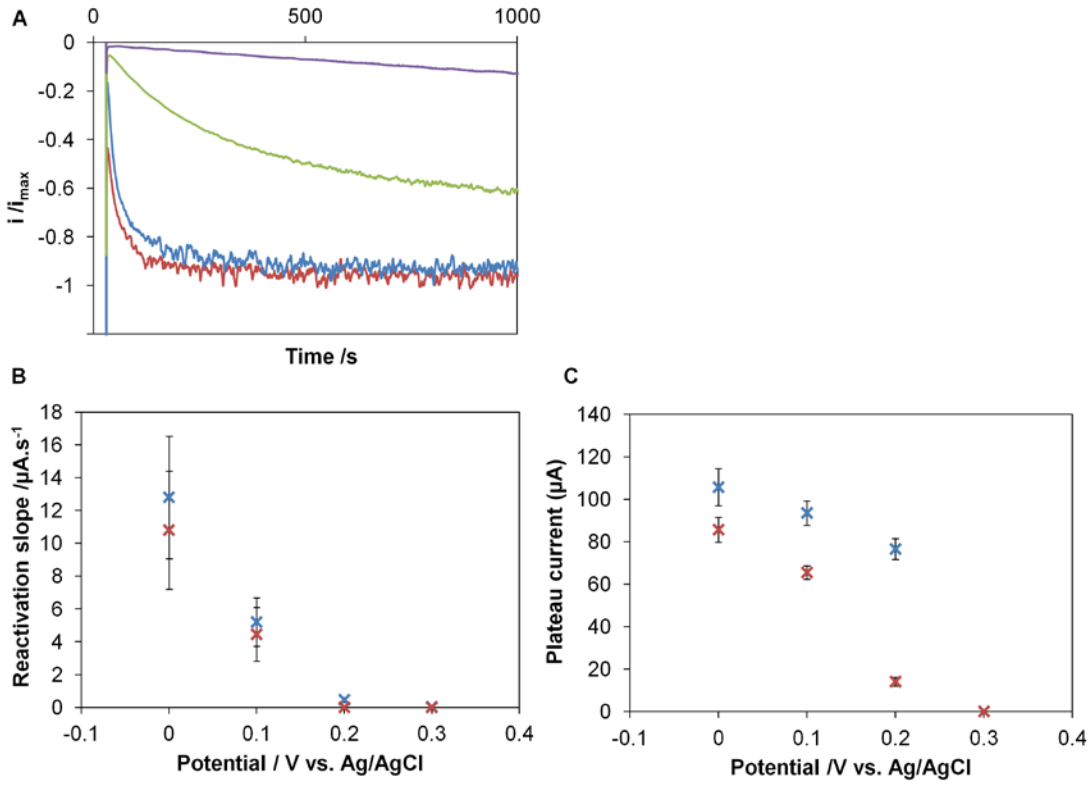


Figure SI6. Influence of electrode potential on *B. pumilus* BOD reactivation. (A) Chronoamperometry experiments in the presence of 200 mM NaCl for E=0V (red curve) ; E=0.1V (blue curve) ; E=0.2V (green curve) and E=0.3V (purple curve). (B) reactivation slopes extracted from the chronoamperometry experiments in the presence of 200 mM NaCl in the electrolyte (red crosses) and after removal of NaCl from the electrolyte (blue crosses). (C) current plateau extracted from the chronoamperometry experiments in the presence of 200 mM NaCl in the electrolyte (red crosses) and after removal of NaCl from the electrolyte (blue crosses). O_2-saturated phosphate-citrate buffer 200-100 mM pH 4; T=25°C.

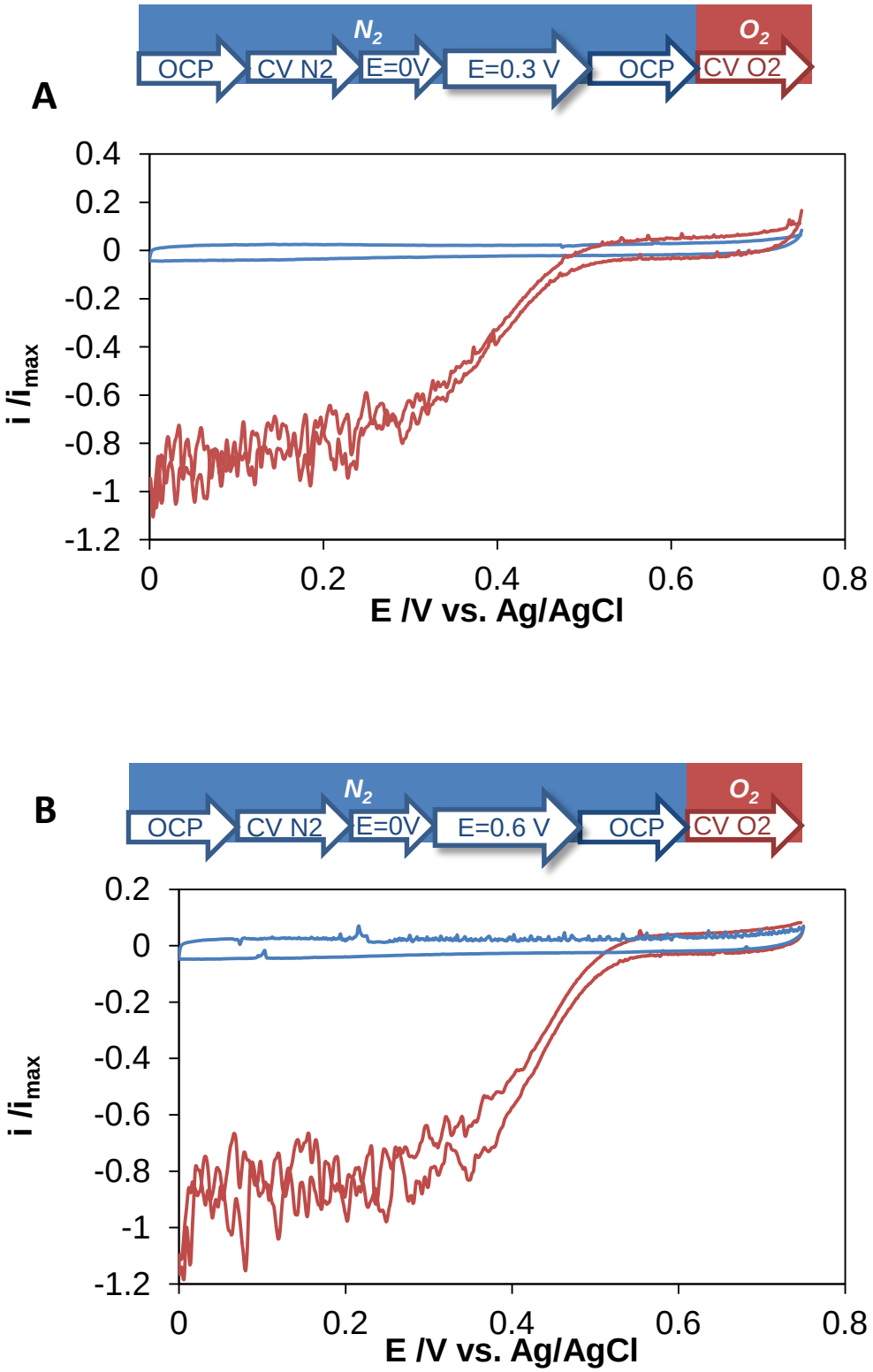
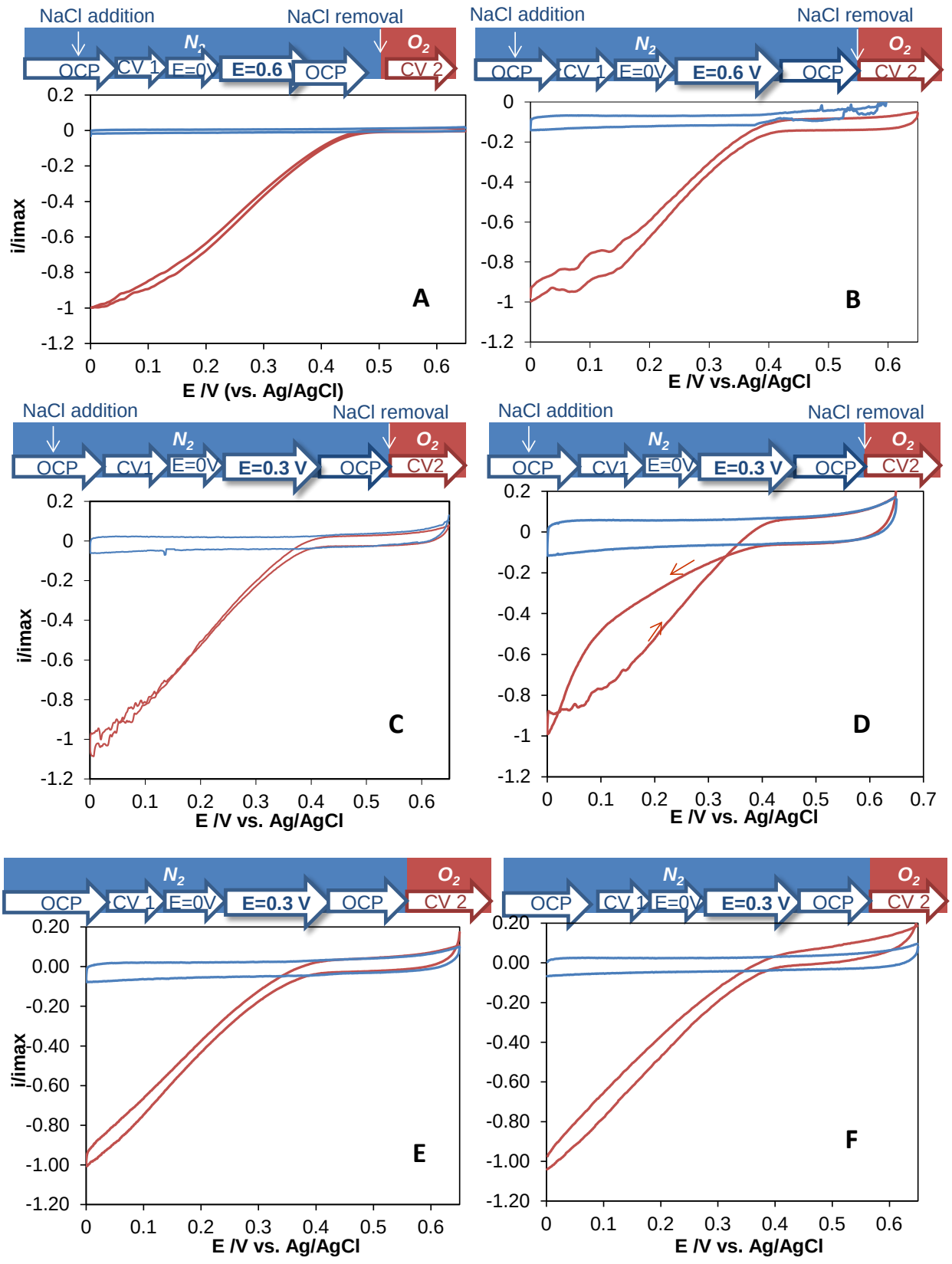


Figure SI7. CV curve at 5 mV.s^{-1} under O_2 after a reductive potential has been applied under N_2, followed by the application of an oxidative potential of +0.3V(A) for 10 minutes or +0.6 V (B) in the absence of NaCl under N_2. O_2-saturated Phosphate-citrate buffer, 200-100 mM pH 4, T = 37 °C, the pyrolytic graphite electrode was modified with carbon nanofibers.


NaCl addition
NaCl removal
N2
O2
OCP
CV 1
E=0V
E=0.6
OCP
CV 2
i/imax
E /V (vs. Ag/AgCl)
A
NaCl addition
NaCl removal
N2
O2
OCP
CV 1
E=0V
E=0.6 V
OCP
CV 2
E /V vs.Ag/AgCl
B
NaCl addition
NaCl removal
N2
O2
OCP
CV1
E=0V
E=0.3 V
OCP
CV2
i/imax
E /V vs. Ag/AgCl
C
NaCl addition
NaCl removal
N2
O2
OCP
CV1
E=0V
E=0.3 V
OCP
CV2
E /V vs. Ag/AgCl
D
N2
O2
OCP
CV 1
E=0V
E=0.3 V
OCP
CV 2
i/imax
E /V vs. Ag/AgCl
E
N2
O2
OCP
CV 1
E=0V
E=0.3 V
OCP
CV 2
E /V vs. Ag/AgCl
F

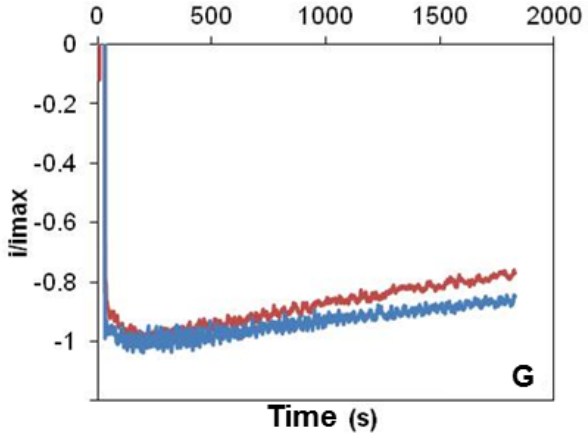


Figure SI8. CV curves at 5 mV.s^{-1} under N_2 (blue curve) and under O_2 (red curve) after an oxidative potential (+0.6V) has been applied for 30 mn (A) or 3 hours (B) in the presence of 200 mM NaCl under N_2.

C- D: same experiment but an oxidative potential of +0.3V has been applied for 30 mn (C) or 2 hours (D) in the presence of 200 mM NaCl under N_2 conditions .

E-F: CV curves at 5 mV.s^{-1} under N_2 (blue curve) and under O_2 (red curve) after + 0.3V has been applied in the absence of NaCl under N_2 for 30 mn (E) or 2 hours (F). (G) Chronoamperometric measurement at E = +0.3 V vs Ag/AgCl as a function of NaCl concentration. 50 mM (blue curve), 200 mM (red curve). O_2-saturated Phosphate-citrate buffer, 200-100 mM pH 7, T = 37 °C, the pyrolytic graphite electrode was modified with carbon nanofibers.