Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

- Supporting Information -

Nanoporous Dual-Electrodes with Millimetre Extensions: Parallelized Fabrication & Area Effects on Redox Cycling

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FABRICATION PROCESS

The fabrication process of the sensor is depicted in Figure S1. In a standard lithography step the structured bottom electrode stack, consisting of 10 nm Ti, 70 nm Pt and 10 nm Ti, is deposited onto a 4-inch silicon wafer (SiMat p (B), <100>, 7 – 21 Ωcm) with 1000 nm of thermally grown oxide (Tempress Systems B.V.). To obtain sufficiently flattened edges of the conducting paths a resist stack consisting of LOR 3B (MicroChem Corp.) and AZ nLOF 2020 (MicroChemicals GmbH) is spin-coated in two steps. The photo resist is structured (Suess MA 6) and both resists are developed in AZ 326 MIF (MicroChemicals GmbH). Following the electron beam evaporation (Pfeiffer PLS 500 Physical Vapor Deposition System) the lift off is performed in EBR PG (MicroChem Corp.). To minimize the chance of redepositions of metal or resist each wafer is washed again in fresh EBR PG, extensively rinsed with bidest and carefully blown dry with nitrogen. In a second deposition step the complete wafer is covered with 10 nm Ti and 200 nm Al (Figure S1c).

Following the layer deposition, the wafer is anodized (Figure S1d) as a whole in 0.3 M oxalic acid. A potential of 40 V is applied between the wafer and a grid of platinum wires. Current densities of about 30 mA cm^{-2} are yield during regular pore growth. As all pores reach the titanium layer the current decreases to about 4 mA cm^{-2} after approximately 6 min. To ensure a full oxidation the voltage is kept up for at least another minute. For the anodization a home-built Teflon cell is used. The cell and the exemplary current trace can be seen in Figure S2.

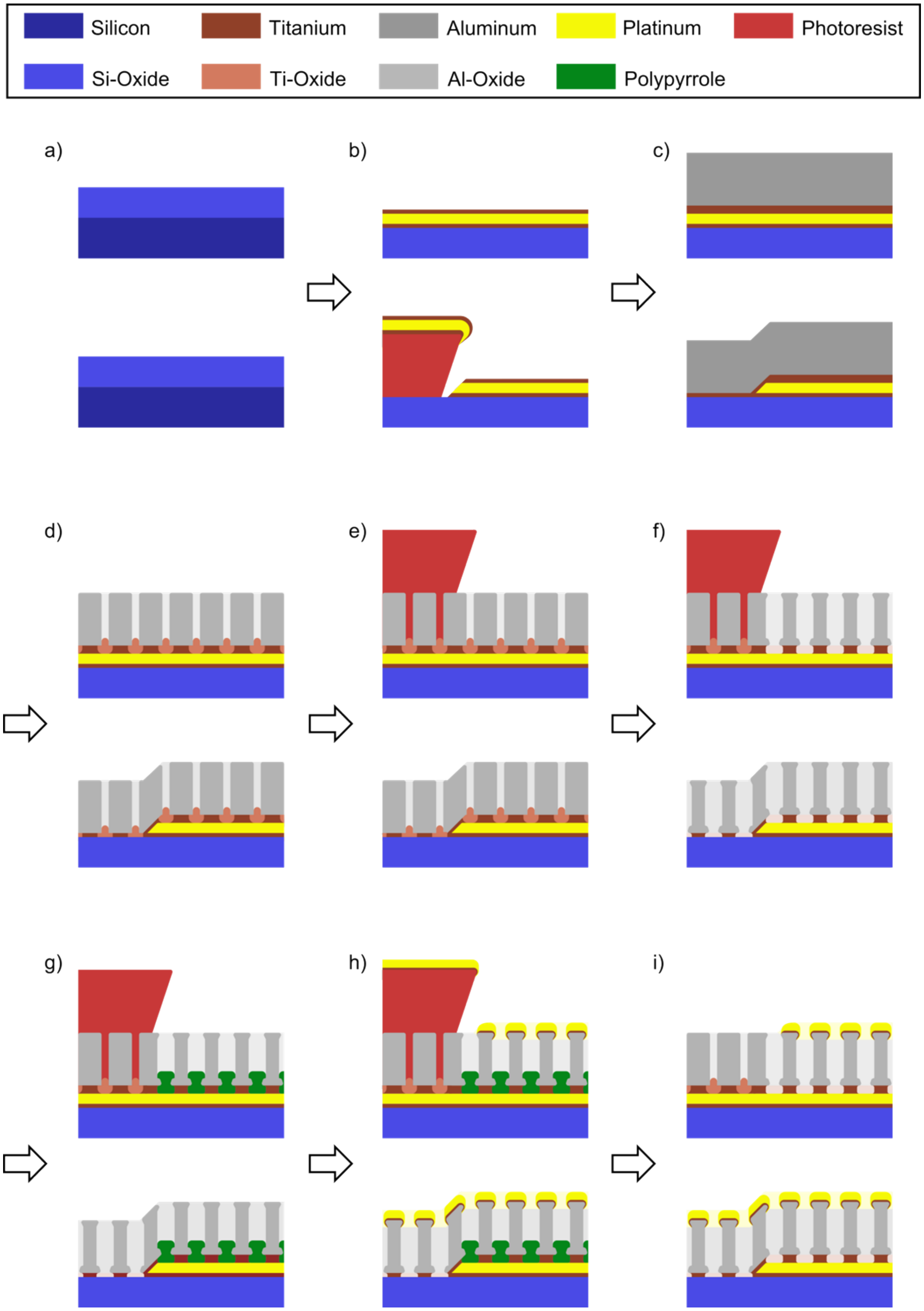

Fig. S1 Fabrication steps of the nanoporous alumina sensor at the boundary areas of the crossing electrodes. Upper and lower sketches show the edge of the top and the edge of the bottom electrode, respectively.

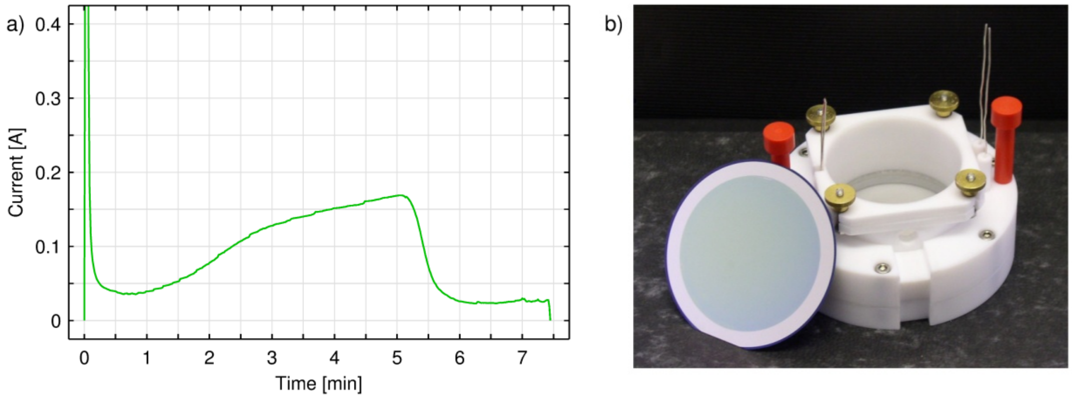

Fig. S2 Current trace obtained from the on-chip aluminum oxidation (Figure S1d) of a structured wafer (a). The initial peak current, which is limited to 1.8 A, is not depicted completely. For the process a home-build Teflon holder is used (b). It is shown here with an unstructured anodized 4”-wafer.

For the subsequent process steps the wafer was selectively covered with negatively processed AZ-5214E photo resist (MicroChemicals GmbH). Only the areas beneath the future top electrode and its feed lines keep exposed (Figure S1e). First, the titanium plugs formed at the alumina pore bottoms are removed in a fresh solution of aqueous 30 wt.% hydrogen peroxide (H_20_2) containing 0.20 M dipotassium phosphate (K_2POH_4) and 0.05 M ethylenediaminetetraacetic acid (EDTA) (Figure S1f). The etching is performed for about 50 min at 50°C. Simultaneously, the alumina pores are widened by the solution. About ten minutes after the observation of homogeneous bubbling the sample is removed from etching bath and cleaned with bidest. Other etches are aqueous solutions of 30 wt.% hydrogen peroxide containing either 0.05 M EDTA and 0.35 M sodium acetate (NaOAc) or 0.35 M 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES buffer). Pore widening is facilitated by 0.15 M oxalic acid ($(COOH)_2$) added via oxalic acid dihydrate.

Within the next step pyrrole is electrochemically deposited into the alumina template onto the underlying Pt layer (Figure S1g). A mixture of 1.8 vol% of pyrrole in a 0.2 M $NaHCO_3$ aqueous solution is used. The deposition is performed with a Bio-Logic VSP 300 and an attached booster kit. A Warner Instruments “Leak-Free Reference Electrode” (WPI) is serves as a reference electrode. After 10 initial voltammetric sweeps between 0 V and 1.5 V vs. Ag/AgCl with 100 mV s^{-1} the maximum potential is applied for 20 min. Potential and current trace are depicted in Figure S3. The cyclic voltammogram in the inlay reveals the typical deposition peak of the first sweep at around 750 mV. This peak is followed by over-oxidation currents, which associate the passivation of the polypyrrole layer. Consequently, the currents for the inverse scan direction are drastically reduced. With an increasing number of scans as well as at the constant potential phase the maximum currents further decrease, indicating a successful passivation.

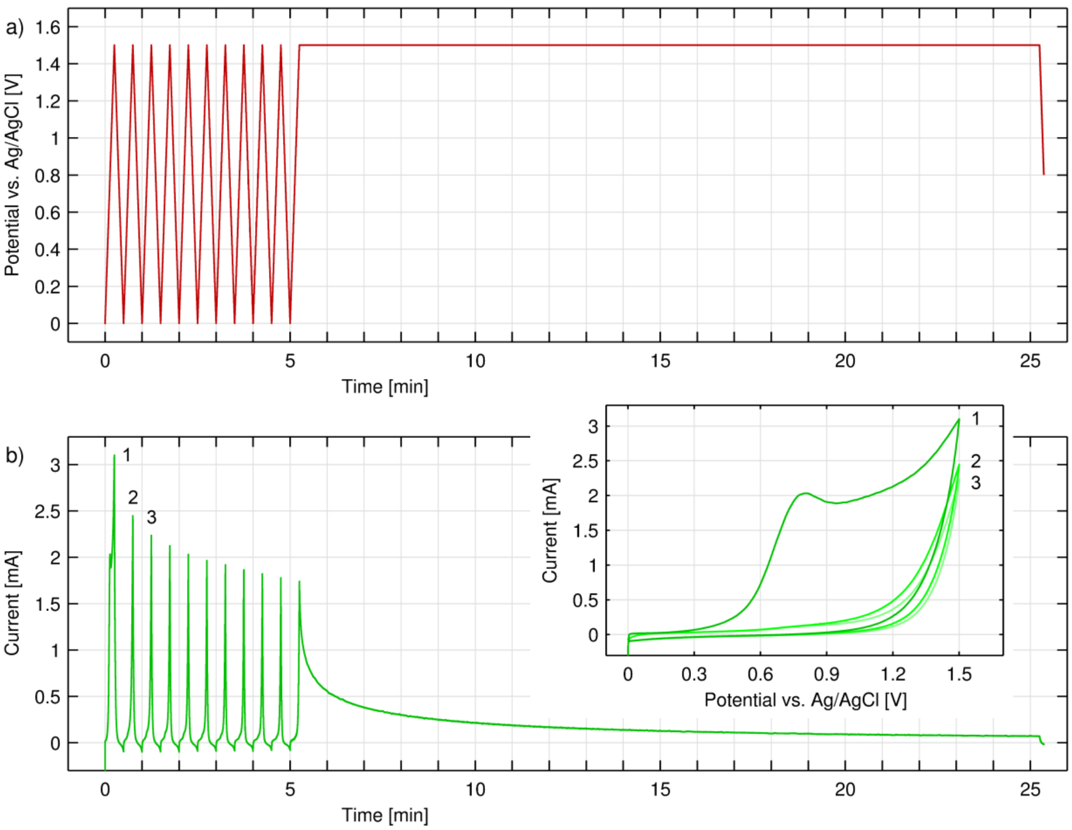

Fig. S3 Potential (a) and current (b) trace of the pyrrole deposition step (Figure S1g). In the inlay the currents of first three sweeps (1-3) are plotted versus the applied potential.

Following the pore-passivation the top electrode stack consisting of 5 nm Ti and 25 nm Pt is evaporated on top of the alumina template (Figure S1h). To strip the structured resist, which is still shielding the non-electrode areas, the wafer is exposed to a bath of acetone and washed in isopropanol. After being covered with a protecting layer of AZ-5214E the wafer is diced to 11×11 mm^2 chips holding one crossing pair of electrodes. Acetone and isopropanol are again used to wash off the resist. For the removal of the polypyrrole encapsulation oxygen plasma is applied in a plasma oven at 0.3 mbar for 5 min (Figure S1i).

Finally, a stack of glass rings is glued onto the sensor using a mixture of dimethylsiloxane and a curing agent (Sylgard 184 Elastomer Kit, Dow Corning GmbH). Hardening of the glue due to polymerization to PDMS is facilitated by baking the chips at moderate temperatures (60°C - 80°C) for about 10 min. If a removable fixation of the glass rings is preferred, AZ photo resist can be used instead of PDMS.

NUMERICAL SIMULATIONS

Geometry		
Parameter	***Value***	***Description***
d_{int}	~ 86 nm	distance between pore centers (interpore dist.)
r_{vol}	45 nm	radius of the simulated cell holding a pore
h_{vol}	400,000 nm	height of volume above the pore (reservoir)
$h_{volfine}$	50 nm	part of reservoir with refined mesh
h_{Pttop}	25 nm	height of top electrode
r_{top}	12 nm	radius of aperture at pore’s top
q_{Pttop}	8 nm	height of top electrode reaching into pore
h_{pore}	375 nm	height of insulator separating electrodes
r_{pore}	20 nm	radius of pore at insulating AlOx
h_{bot}	36 nm	height of tapering of insulator’s lower end
r_{bot}	12 nm	radius of tapering at insulator’s lower end
h_{Tibot}	10 nm	height of bottom adhesion layer
r_{Ptbot}	35 nm	radius of aperture at bottom electrode
L_{por}	3 mm	edge length of active dual electrode area

Electrochemistry		
Parameter	***Value***	***Description***
f	f = F / RT	
F	96485.3365 C mol^{-1}	Faraday constant
R	8.3144621 J mol^{-1} K^{-1}	universal gas constant
T	298 K	temperature
α	0.50	transfer coefficient
k_s	8.5×10^{-2} cm s^{-1}	heterogeneous electron transfer constant
E_0	350 mV	redox potential vs. Ag/AgCl
$D_{red,}$ D_{ox}	6.32×10^{-6} cm^2 s^{-1} 7.63 10^{-6} cm^2 s^{-1}	distinct diffusion constants for reduced / oxidized species
$c_{red,}$ c_{ox}	–	concentration of reduced / oxidized species
c_{red}^0, c_{ox}^0	330 µM 0 µM	initial concentration of reduced / oxidized species

Voltammetry		
Parameter	***Value***	***Description***
$E_{top,bot}$	E_{min}, E_{max}, E_{sw}	potential of top / bottom electrode
E_{sw}	E_{min} … E_{max}	potential of sweeping electrode
$E_{min,}$ E_{max}	50 mV 650 mV	minimum / maximum potentials vs. Ag/AgCl
v	20 cm s^{-1}	sweep rate
E_{step}	10 mV	voltage steps
t_{step}	0.5 cm s^{-1}	time stepping

Table S1 Parameters and their typical values used within the numerical calculations.

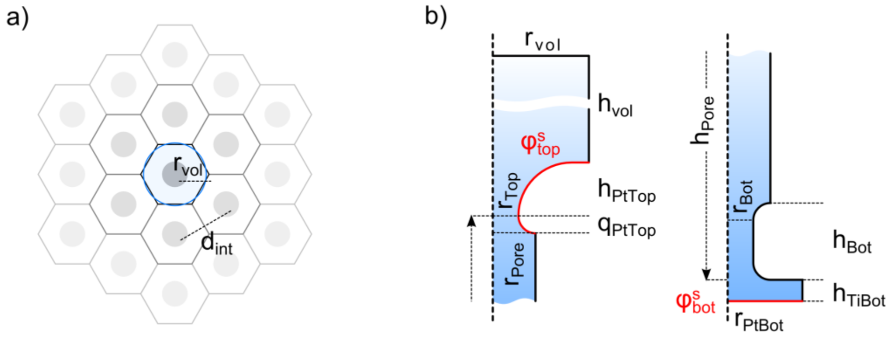

Fig. S4 Approximation of the nanoporous sensor by single identical domains (a) as well as the assumed radial symmetric geometry of a single pore and the adjacent reservoir (b).