Supplementary Material

Synthesis of plate Ti$_4$O$_7$ ceramic electrode

Plate Ti$_4$O$_7$ ceramic electrode was synthesized through a high temperature sintering process as described in a prior study[1]. In brief, TiO$_2$ powder was heated at 950 °C and reduced to Ti$_4$O$_7$ powder under controlled H$_2$ flow. The Ti$_4$O$_7$ powder was mixed (0.5%, m/m) with polyacrylamide/polyvinyl alcohol (95/5, m/m) to form a slurry that was then spray-dried to form ceramic granulates. The ceramic granulates were then pressed to make a ceramic preform that was dried and then sintered at 1350 °C in a vacuum for 11 h to form a bulk electrode.

MS analysis

PFOS was analyzed using a Waters Acquity UPLC system coupled with Xevo TQD tandem mass spectrometry (UPLC/MS/MS) with electrospray ionization (ESI) source (Milford, MA, USA). MS was operated at negative ESI. A Waters Acquity UPLC BEH C18 column (50 mm × 2.1 mm, i.d., 1.7 µm) was used for separation. The program of the delivery solvent consisting of methanol and water (both with 5 mM ammonium acetate) was set as follows: methanol increasing linearly from 40% to 80% in the first 4 min, and then decreasing to 40% at 5 min. The flow rate was 0.3 mL/min. Detailed operational parameters were: capillary voltage 1.14 kV, cone voltage 60 V, source temperature 400 °C, desolvation temperature 550 °C, cone gas flow 50 L/h, and desolvation gas flow 500 L/h. PFOS and its isotope labeled standard were identified using multiple reaction monitoring (MRM) mode based on the transition patterns: m/z = 499 > 80 for PFOS, and m/z = 507 > 99 for M8PFOS. Quantification was achieved by the ratio of the MRM signal of the chemical to that of the internal standard in reference to a five-point calibration curve.

ClO$_3^-$ and ClO$_4^-$ were also analyzed using the UPLC/MS/MS at ESI negative mode. An isocratic elution consisting of methanol and water was used as mobile phase (50/50, v/v). The flow rate was 0.3 mL/min for a total elution time of 4 min. Detailed instrument setup was the same as above. They were analyzed at MRM mode based on the transition m/z = 83 > 67 and m/z = 99 > 83 for ClO$_3^-$ and ClO$_4^-$, respectively. ClO$_3^-$ and ClO$_4^-$ were quantified with an external calibration curve.

Fluoride Analysis

A standard addition approach was used to measure fluoride (F$^-$) concentration using a F$^-$ ion selective electrode (Thermo Scientific^{TM} Orion^{TM})[2]. 5 mL aliquots of a sample were pipetted into 5 mL volumetric tubes. Exactly 0, 0.05, 0.10, 0.15, and 0.25 mL of a standard solution (C_S) containing 100 mg/L of F$^-$ were added to each. After dilution to volume, the meter response S for each of the five solutions was measured with a F$^-$ selective electrode.

Based on the F$^-$ concentration, a defluorination ratio (F$_r$) was calculated using Eq. (1):

$$F_r = \frac{C_{F,t} - C_{F,0}}{(C_0 - C_t) \times 17} \times 100\% \tag{1}$$

where $C_{F,t}$ and $C_{F,0}$ are the concentrations of F$^-$ in treatment solution at time t and 0, respectively; C_0 and C_t are the concentrations of PFOS at time 0 and t, respectively, and the factor 17 corresponds to the number of fluorine atoms in a PFOS molecule.

Mass Transfer Rate

The limiting current technique was used to estimate the limiting current density in a solution containing 10 mM $K_4Fe(CN)_6$ and 10 mM $K_3Fe(CN)_6$, and 100 mM KH_2PO_4 background electrolyte with Ti_4O_7 (10 cm × 5 cm) anode. The limiting current density was determined to be J_{lim} = 53.8 A/m^2. The mass transfer rate constant for $Fe(CN)_6^{4-}$ to the Ti_4O_7 electrode surface was calculated using Eq. (2) to be $k_{m,o}$ = 5.58×10^{-5} m/s[3].

$$k_{m,o} = \frac{J_{lim}}{nFC} \tag{2}$$

In Eq. (2), n=1 and F is the Faraday constant (96485 C/mol). Then, Eq. (3) was used to calculate the mass transfer rate constant, $k_{m,i}$, of PFOS and TCE.

$$k_{m,i} = k_{m,o} \left[\frac{D_i}{D_o}\right]^{\frac{2}{3}} \tag{3}$$

The relevant diffusion coefficients Di of PFOS and TCE were 4.70×10^{-10} and 8.16×10^{-10} m^2/s, respectively[4, 5]. The relevant diffusion coefficients D_o of $Fe(CN)_6^{4-}$ was 7.43×10^{-10} m^2/s[6]. Based on Eq. (3), the mass transfer rate constant of PFOS and TCE were calculated to be 4.11×10^{-5} and 5.94×10^{-5} m/s, respectively.

Effective Electro-active Surface Area

Voltammetric charge ($q*$) is related to the specific surface area and the amounts of electro-active sites of an electrode. Cyclic voltammetry was performed within the potential range of 0.7-1.7 V (vs. SHE) in 100 mM Na_2SO_4 solution at different sweep rates to test $q*$ and the distribution of electro-active sites on the outer and inner surface of the porous Ti_4O_7 ceramic electrode[7]. Specifically, the ratio between the inner voltammetric charge (q_{I*}) and the total voltammetric charge (q_{T*}), also known as the electrochemical porosity (q_{I*}/q_{T*}), was calculated to be 98.26% (Table S1)[7]. The roughness factor (Rf), defining the electroactive area per geometrical area, was found to be 344.5 ± 15.7 for the porous Ti_4O_7 ceramic electrode. The effective electro-active surface area was calculated to be 467.37 cm^2. Detail calculation procedure can be found in our previous report[1].

References

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