Supporting Information

Auto-oxidation of Redox-Electrodes for the Selective Recovery of Platinum Group Metals

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Experimental Procedures

Synthesis and characterization of redox polymers

Polyvinyl ferrocene (PVF) was bought from Polysciences Inc.

Synthesis of poly(3-ferrocenylpropyl methacrylamide) (PFPMAm) followed previously reported method¹. The monomer (FPMAm) was synthesized by following procedure: 3 g Ferrocenyl propylamine was dissolved in 80 mL dry dichloromethane in a flask then added 1.37 g triethylamine to generate the orange solution. After that, cooled the solution in an ice bath for 30 minutes and slowly added 2.09 g methacrylic anhydride at same time. Afterward, removed the ice bath and stirred at room temperature for another 16 hours then washed with saturated aqueous NaHCO₃ solution, water, and brine. The organic phase was then dried with MgSO4, and the solvent was evaporated after filtration, yielding the crude product as a brownish oil. The product was purified by flash chromatography (silica column and hexane/EtOAc gradient), yielding FPMAm orange solid. For polymerization, 5 g FPMAm and 26.4 mg Azobisisobutyronitrile (AIBN) were dissolved in 1,4-Dioxane (50 mL). The mixture was degassed by bubbling with argon for 15 minutes and heated to 60°C for 16 hours. The polymer was precipitated in MeOH (500 mL) and filtered. The polymer was dissolved in 50 mL of THF, precipitated again in MeOH and dried under reduced pressure, yielding 3.50 g (70%) PFPMAm as an orange solid. M_n = 19.6 kg mol⁻¹, M_w = 44.4 kg mol⁻¹, D = 2.26. Derived from Gel Permeation Chromatography (GPC)

2-((1-ferrocenylethyl)(methyl)amino)ethyl methacrylate (FEMA) was synthesized according to literature protocols². For polymerization, 512 mg FEMA and 4.73 mg AIBN were dissolved in 1, 4-dioxane (4.1 mL). The solution was purged with argon for 15 minutes and stirred at 60 °C for 20 hours. The polymer was precipitated in MeOH (41 mL) and filtered. The polymer was dissolved in small amount of THF, precipitated again in MeOH and dried under reduced pressure, yielding 369 mg (66%) PFEMA as a yellow solid. GPC: Mn = 10.51 kg mol⁻¹, Mw = 16.419 kg mol⁻¹, \overline{D} =1.56. Derived from GPC.

Synthesis of 2-(methacryloyloxy)ethyl ferrocenecarboxylate (FcMA) followed literature protocol³. For polymerization, FcMA (10.00 g) and AIBN (48.0 mg) were dissolved in 1,4-Dioxane (60 ml). The mixture was degassed by bubbling with argon for 15 minutes and heated to 60°C for 16 hours. The polymer was precipitated in MeOH (600 ml) and filtered. The polymer was dissolved in 50 mL of THF, precipitated again in MeOH and dried under reduced pressure, yielding 8.14 g (81%) PFcMA as an orange solid. Mn = 48.5 kg mol⁻¹, Mw = 124.7 kg mol⁻¹, D = 2.57. Derived from GPC.

Electrode preparation and characterization

All Redox polymers-CNT were prepared by drop-coated via pipette with redox polymer ink solution. The polymer-CNT ink solution was prepared by previously reported methods. Solution "A" containing 80 mg redox polymer in 10 mL chloroform while solution "B" containing 40 mg multiwalled CNT in 10 mL chloroform. Both solutions were sonicated for 1 hour in icy water. Two solutions were mixed in 1:1 ratio and sonicated for 1 hour in icy water and get solution "A+B", the ink solution used in this research. Carbon paper (Toray 030) was cut into 3*1 cm strips and drop-coated (50 µL) via pipette to fully cover 1*1 cm of carbon paper. The polymer-CNT–coated electrode was then dried at room temperature and yielded a 0.4 mg of polymer-CNT coating consisting of 0.2 mg of redox polymer.

Cyclic voltammetry of six cycles at 20 mV/s (-0.2 to 0.8 V versus Ag/AgCl) was run with BioLogic SP-200 singlechannel potentiostat in 2 mL of 20 mM NaClO₄ (1*1 cm polymer-CNT coated carbon paper working, plain carbon paper counter, and Ag/AgCl reference).

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were carried out by using a ThermoFisher Axia ChemiSEM-EDS in high-vacuum SE mode at 20.000 kV in Frederick Seitz Materials Research Laboratory Central Research Facilities, University of Illinois Urbana Champaign. SEM was for electrode surface and morphology characterization while EDS was used to qualitatively identify the presence of carbon, iron, oxygen, nitrogen, iridium, and palladium of the electrode surface before and after adsorption or desorption.

X-ray photoelectron spectroscopy (XPS) was performed by MSE Supplies LLC to analyze the surface component. C 1s, Fe 2p, Rh 3d, Ir 4f, and Pt 4f were characterized. The XPS spectra deconvolution was processed using CASA XPS software (UIUC license). XPS binding energies were referenced to C 1s as 284.8 eV.

Electrosorption, energy consumption, and separation factor tests

Electrosorption/release and separation factor tests were conducted with three-dimensional (3D) print electrochemical cells similar as previously reported. The 3-D printed electrochemical cell was constructed with polypropylene with a layer thickness of 0.1 mm and a hole with radius for kinetic sampling. All electrosorption/release and separation factor tests were performed in a printed cell with a 3*1 cm redox polymer-CNT working electrode (1*1 cm coated), a 3*1 cm plain carbon paper counter electrode, a Ag/AgCl reference electrode, and a small stir bar. For electrosorption/release tests, five cycles of cyclic voltammetry from -0.2 to 0.8 V at 20 mV/s were run in 20 mM NaClO4 solution with BioLogic SP-200 single-channel potentiostat before the electrosorption test to remove the surface impurity and stopped at zero current to make redox polymers fully reduced. After that, 2 mL of 1 mM PGMs anions (H2IrCl6, K3IrCl6, H2PtCl6, Na3RhCl6, K2PdCl4, K2Ru(NO)Cl5, Sigma-Aldrich) and 20 mM NaClO4 were added into the printed cell as analytical solution unless otherwise specified. Open circuit potential or +0.8 V versus Ag/AgCl were applied onto polymer-CNT electrode for 1 hour for electrosorption unless otherwise specified. Regeneration of polymer-CNT redox electrode was done by applying +0.2 V versus Ag/AgCl onto polymer-CNT electrode for 1 hour in clean 20 mM NaClO4 solution. Current and potential of working electrode and Counter electrode were recorded by the potentiostat during electrosorption and release. For kinetic adsorption/release tests, setup was same as previously discussed except 50 µL of analytical solution was taken for analyzing at 1, 2, 5, 10, 15, 30, 45, 60 minutes.

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Agilent 5110) were utilized for quantifying concentration of iridium, platinum, rhodium, palladium, and ruthenium. A HCl dilution solution (5 wt %) was prepared from 38% HCl (Thermo Fisher Scientific) and used to dilute calibration standards and Aliquots. ICP calibration standards (Ir, Pt, Rh, Pd, Ru standard for ICP TraceCERT, 1000 mg/liter hydrochloric acid) were diluted with 5 wt% hydrochloric acid to make the calibration curve. Uptake was calculated using the following equation:

$$Uptake = \frac{c_0 - c}{m_{polymer}} V$$
(Equation 1)

Where C_0 was the initial molar concentration of the analyte (Ir, Pt, Rh, Pd, Ru), C was the molar concentration of analyte during or after adsorption, V was the volume of the solution in the cell while $m_{polymer}$ was the number of polymer (in mole) on the working electrode.

Regeneration efficiency was calculated using the following equation:

$$Regeneration \ efficiency = \frac{\frac{C_{release}}{m_{polymer}} v_{release}}{U_{ptake}} * 100\%$$
(Equation 2)

Where $C_{release}$ was the molar concentration of analyte during or after desorption, $V_{release}$ was the volume of the solution in the cell during releasing.

Energy consumption was calculated using the following equation:

$$Energy \ consumption = \frac{\int (E_{anode} - E_{Cathode}) * I * \Delta t}{Uptake \ or \ release}$$
(Equation 3)

Where E_{anode} was the potential of anode and $E_{cathode}$ was the potential of cathode during adsorption or desorption, I was the current at each recorded point during adsorption or desorption, Δt was the recorded time interval (0.1 second) between each measured potential and current.

For separation factor tests, two different types of 1 mL of PGMs anions were mixed with 20 mM NaCl as supporting electrolyte for analytical solution. electrochemical cell setup and methods were same as previously discussed. Separation factors were calculated by the following equation:

$$\alpha_{A, B} = \frac{N_{A, ads} / C_{A, sol}}{N_{B, ads} / C_{B, sol}}$$
(Equation 4)

Where $N_{A, ads}$ and $N_{B, ads}$ were the molar quantities of PGMs anions A and B adsorbed and $C_{A, sol}$ and $C_{B, sol}$ were the concentration of PGMs anions in solution during or after adsorption. If the separation factor is higher than 1, it means that a redox polymer has higher selectivity toward species A rather than B (indicated by red colored square); if separation factor is lower than 1, it means that a redox polymer has higher selectivity toward species B rather than A (indicated by blue colored square).

UV-Vis spectroscopy (Cary 60, Agilent) was carried out for quantifying the concentration of iridium(III) and iridium(IV) in the aqueous solution that iridium(IV) has a significant peak at 520 nm while iridium(III) does not⁴.

Chloralkali electrolysis

The setup for chloralkali electrolysis was same as electrosorption tests. For normal chloralkali electrolysis, carbon paper was set as both working and counter electrode and applied constant -100 µA for 15 minutes in 25 wt% NaCl aqueous solution. For chloroalkali electrolysis with PVF-CNT, PVF-CNT was pre-oxidized at 0.8 V vs Ag/AgCl in NaClO4 for 10 minutes then transfer to 25 wt% NaCl aqueous solution works as working electrode while the counter electrode is carbon paper and -100 µA constant current was applied for 15 minutes. Current, potential of working electrode and counter electrode were recorded with potentiostat.

In-situ electrosorption analysis

In-situ electrosorption analysis was carried out using Electrochemical quartz crystal microbalance (EQCM, BioLogic BluQCM QSD (QSD-TCU)) to measure the frequency change with Au-coating 5 MHz quartz crystal, with a piezo electroactive area of 0.2 cm² (diameter: 14 mm, polished finish, AW-R5CUP, BioLogic) working electrode, platinum wire counter, and Ag/AgCl (in 3M NaCl) reference electrode. The working electrode was spun coated (2000 rpm for 1 min with acceleration of 1000 rpm) with 50 μ L PVF solution (7.5 mg/mL in chloroform) and 1 mM PGMs anions analyte solution was added to the electrochemical cell before analyzing. The mass change was determined by Sauerbrey equation:

$$\Delta f = \frac{-2f_0^2 \Delta m}{A \sqrt{\mu_i \rho_i}}$$
(Equation 5)

Where Δf is the change of frequency, f_0 is the resonant frequency of the quartz crystal, A is the piezo electroactive area, μ_i is the shear modulus of the quartz (2.947 × 1011 g cm⁻¹ s⁻²), ρ_i is density of the quartz (2.648 g cm⁻³), and Δm is the mass change.

Catalytic converter recovery

A catalytic converter from a 2014 Scion Tc was purchased new from Toyota, and the internal PGM-coated catalyst material was removed from the stainless-steel tubing with a grinding wheel. 663 g of catalyst material was recovered from the catalytic converter, and the material was finely ground with mortar and pestle. In a typical digestion, 1 g of crushed catalyst material was added to 25 mL of 38% hydrochloric acid. Chlorine gas was generated in-situ by adding 5 mL of a 9% sodium hypochlorite solution. The vessel was sealed shut with Teflon tape and left to stir for 24 hours. The remaining solids were filtered out, and the clear red digestion solution was transferred to an evaporating dish and left to evaporate at 40 °C until only 1 mL of solution remained to remove excess chlorine gas and HCl. Finally, 24 mL of DI water was added to the 1 mL concentrate for a final catalyst digestion solution. The solution was analyzed with ICP-OES and its composition is shown in Table S1. Adsorption experiments were carried out in a similar manner as previous tests: a PVF-CNT electrode with 0.2 mg of PVF and a 1x1 cm area was placed in 1.5 mL of digested catalyst solution along with Ag/AgCl reference and carbon paper counter electrode. The cell was operated either at open circuit potential or at a constant 0.8 V vs Ag/AgCl for 1 hour. ICP-OES was used to determine the change in component composition before and after adsorption.

Results and Discussion

Catalyst Mass:	1	g
Solution Volume:	2	
Component	Digestion Concentration	Loading
Sc		2 1
Y	1 4	4
Ru	1	4
Rh	4	1 1
Pd	1 44	1
La	2 14	2
Ce		1
Pr	2 1	4
Sm		1 1
Ir	2	
Pt		

 Table S1. 2014 Scion Tc Catalytic Converter Composition



Fig. S1 Cyclic voltammogram (fifth cycle, 20 mV/s scan rate in 20 mM NaClO₄), half potentials and structures of polymers. (a) PVF. (b) PFPMAm. (c) PFEMA. (d) PFcMA.



Fig. S2 SEM-EDS images of PVF-CNT, PFPMAm-CNT, PFEMA-CNT, and PFcMA-CNT on carbon paper.



Fig. S3 Iridium concentration profile of 1 mM H_2IrCl_6 (20 mM NaClO₄ as supporting electrolyte) adsorption at OCP with 0.4 mg redox polymers-CNT (0.2 mg redox polymer with 0.2 mg CNT) or 0.2 mg CNT only.



Fig. S4 Iridium uptake profile of 1 mM H₂IrCl₆ (20 mM NaClO₄ as supporting electrolyte) adsorption at OCP with 0.4 mg PVF-CNT (0.2 mg PVF with 0.2 mg CNT) or 0.2 mg CNT only.



Fig. S5 Potential profile of PVF-CNT at OCP in 1 mM H2IrCl6 with 20 mM NaClO4 or 20 mM NaClO4 only.



Fig. S6 Potential profile of counter electrode (bare carbon paper) in 1 mM H₂IrCl₆ adsorption at OCP.



Fig. S7 2 hours platinum adsorption with supporting electrolyte. (a) Adsorption kinetics for platinum with four redox polymers at open circuit potential (0.2 mg polymer in 1 mM H_2PtCl_6 and 20 mM NaClO₄). (b) Potential profile of four redox polymers during platinum adsorption.



Fig. S8 Pt 4f XPS of PVF-CNT after H₂PtCl₆ adsorption at OCP.



Fig. S9 Fitting of iridium kinetic adsorption with redox polymers-CNT. (a) First order fitting of PFPMAm-CNT. (b) First order fitting of PVF-CNT. (C) Second order fitting of PFEMA-CNT. (d) First order fitting of PFcMA-CNT.



Fig. S10 Iridium and ruthenium uptake profile of H₂IrCl₆ and K₂RuCl₅(NO) binary mixture (0.5 mM for each PGMs salt, 20 mM NaCl as supporting electrolyte) with 0.4 mg PFcMA-CNT (0.2 mg PFcMA with 0.2 mg CNT) at OCP.



Fig. S11 SEM-EDS images of Pd adsorbed (1-hour adsorption at OCP in 1 mM K₂PdCl₄ solution with 20 mM NaCl as supporting electrolyte) PVF-CNT (working electrode) and carbon paper (counter electrode) after 1-hour 0.2 V vs Ag/AgCl desorption in 20 mM NaClO₄.



Fig. S12 UV-Vis spetra of 0.045 mM H₂IrCl₆, 0.045 mM K₃IrCl₆, and the release solution (0.2 V applied potential for 1 hour release in 20 mM NaClO₄ after adsorbed for 1 hour at open circuit potential, concentration was around 0.045 mM of iridium).



Fig. S13 Adsorption and release profile of iridium with PVF-CNT (1 mM H_2IrCl_6 in 20 mM NaClO₄ for adsorption with 0.2 mg PVF-CNT at open circuit potential, desorbing in 20 mM NaClO₄ at 0.2 V vs Ag/AgCl after adsorption).



Fig. S14 Multi cycles adsorption and release of H₂IrCl₆ with PVF-CNT (each cycle was carried by out adsorbing 1 mM H₂IrCl₆ solution with 20 mM NaClO₄ as supporting electrolyte for 30 minutes with 0.2 mg PVF-CNT at open circuit potential and desorbing in 20 mM NaClO₄ at 0.2 V vs Ag/AgCl applied potential after adsorption for 30 minutes).



Fig. S15 1 hour Ir(IV) and Ir(III) adsorption with 20 mM NaCl as supporting electrolyte. (a) Adsorption kinetics for iridium with PVF-CNT at open circuit potential (0.2 mg polymer in 1 mM H₂IrCl₆ or K₃IrCl₆ and 20 mM NaCl). (b) Potential profile of PVF-CNT during Ir(III) adsorption.



Fig. S16 EQCM result of iridium adsorption with PVF (1 mM H₂IrCl₆ adsorption for 1 hour with PVF at open circuit potential).



Fig. S17 EQCM result of platinum adsorption/release multicycles with PVF (1 mM H₂PtCl₆ adsorption for 1 hour with PVF at open circuit potential and release at 0.2 V versus Ag/AgCl for 10 minutes, repeating for 3 times).



Fig. S18 Iridium uptake and potential profile of 1 mM H₂IrCl₆ (20 mM NaClO₄ as supporting electrolyte) adsorption at OCP with different PVF-CNT (1:1 in mass ratio) mass loading. (a) Iridium uptake of different PVF-CNT mass loading. (b) Potential profile of different PVF-CNT mass loading at OCP.



Fig. S19 Cyclic voltammetry of PVF-CNT in 20 mM NaCl at 20 mV/s scan rate.



Fig. S20 Supporting electrolyte effect for iridium adsorption with PVF-CNT. (a) Iridium uptake profile at open circuit potential with PVF-CNT with 20 mM different supporting electrolyte or without electrolyte. (b) 1-hour iridium uptake at OCP with 20 mM supporting electrolyte or without electrolyte and regeneration efficiency of PVF-CNT (desorption in 20 mM NaClO₄ with 0.2 V vs Ag/AgCl applied for 1-hour).



Fig. S21 Potential profile of PVF-CNT (working electrode) and counter electrode (carbon paper) in catalytic converter leach solution at open circuit potential adsorption.



Fig. S22 Normalized energy consumption for oxidizing PVF-CNT at 0.8 V vs Ag/AgCl chronoamperometry adsorption in catalytic converter leach solution.



Fig. S23 Energy consumption of chloroalkali electrolysis in 25 wt% NaCl aqueous solution by using carbon paper or PVF-CNT as cathode (-100 μ A constant current was applied).



Fig. S24 Chloralkali electrolysis with PVF-CNT. (a) Cathode potential of PVF-CNT and carbon paper in chloroalkali electrolysis. (b) Overall cell potential of chloroalkali electrolysis in 25 wt% NaCl aqueous solution by using carbon paper or PVF-CNT as cathode.



Fig. S25 Pictures of 3-D printed electrochemical cells. (a) Side view of the 3-D cells and the cap. (b) Top view of the cells and the cap.



Fig. S26 XPS results of PGM standards (samples were prepared by dropping 50 μ L of 1 mM PGMs salt aqueous solution on carbon paper and dried to remove the water). a) Ir 4f XPS spectra of H₂IrCl₆, K₃IrCl₆, electroseposited of irdium on carbon paper after applied -1.0 V versus Ag/AgCl for 30 minutes. b) Pt 4f XPS spectra of H₂PtCl₆, K₂PtCl₄, electroseposited of platinum on carbon paper after applied -1.0 V versus Ag/AgCl for 30 minutes. c) Rh 3d XPS spectra of K₃RhCl₆ and electroseposited of rhodium on carbon paper after applied -1.0 V versus Ag/AgCl for 30 minutes.



Fig. S27 Molecular weight distribution of PFPMAm. Determined by GPC in NaCl/TFA using P2VP calibration.



Fig. S28 ¹H-NMR spectrum of PFPMAm (500 MHz, CDCl₃).



Fig. S29 Molecular weight distribution of PFEMA. Determined by GPC in DMF/LiBr using PMMA calibration.



Fig. S30 ¹H-NMR spectrum of PFEMA (500 MHz, CDCl₃).



Fig. S31 Molecular weight distribution of PFcMA. Determined by GPC in THF/LiBr using PS calibration.



Fig. S32 ¹H-NMR spectrum of PFcMA (500 MHz, CDCl₃).

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