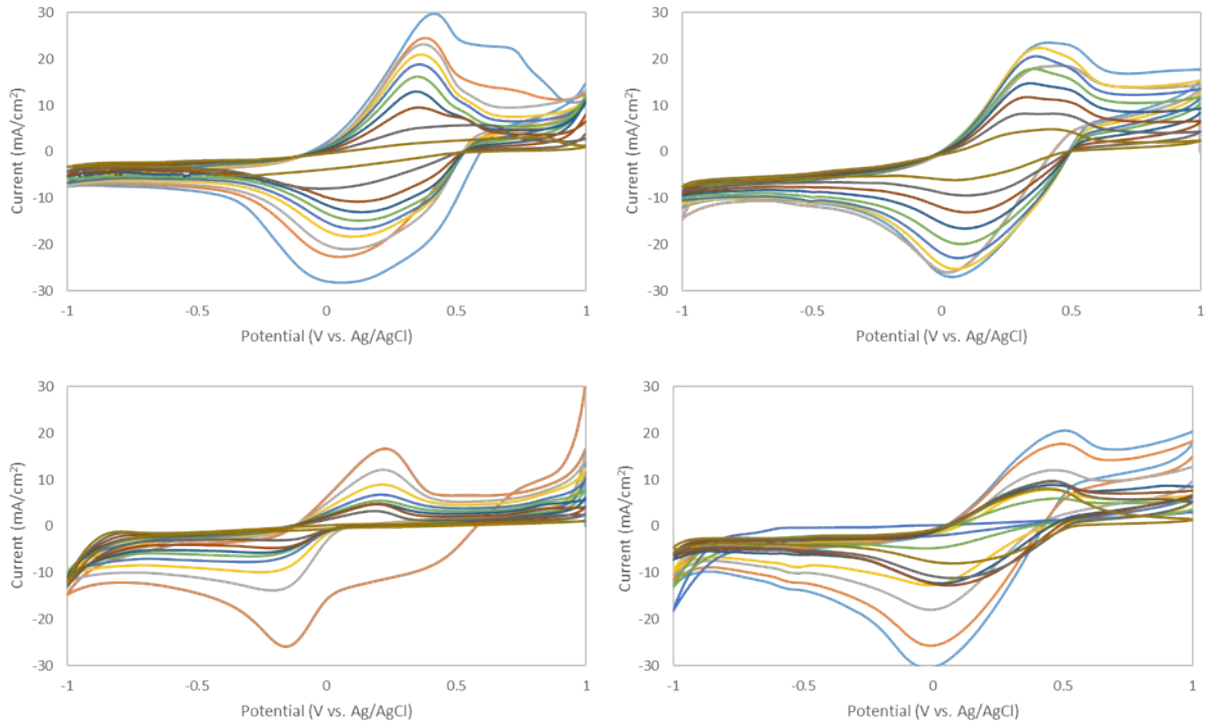
Electronic Supplementary Material (ESI) for Nanoscale.


Supplemental Figures

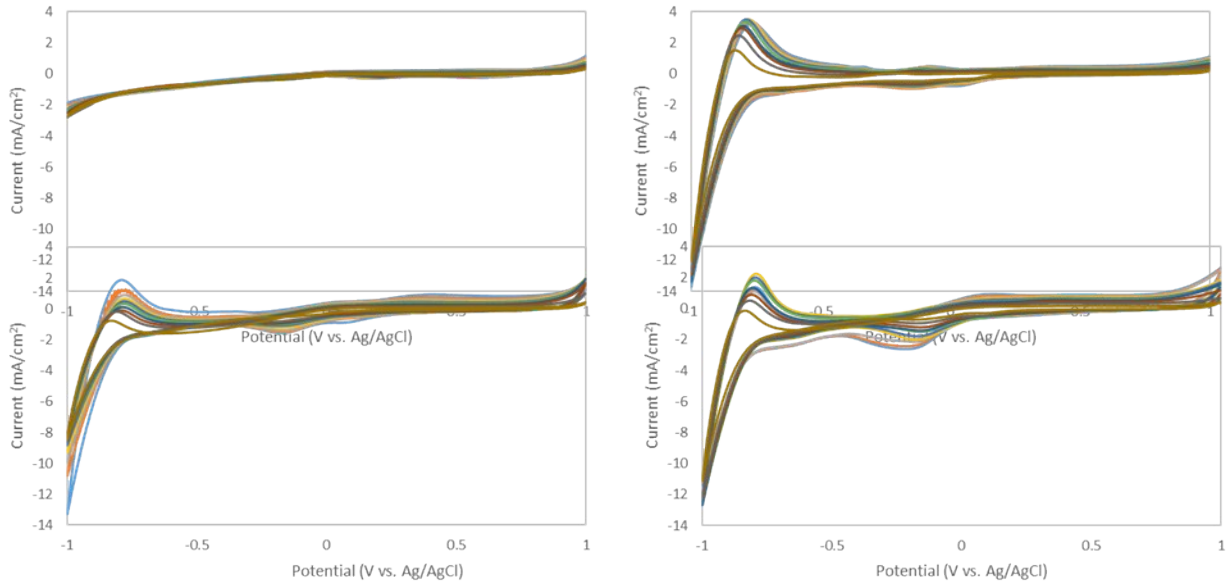


**Figure S1**. Cyclic voltammograms for (A) TFE-Au, (B) TFE-Pt, (C) TFE-Au|Pt, (D) TFE-Pt|Pt, (E)TFE-Au|PAn-Cl, (F) TFE-Pt|PAn-Cl, (G)TFE-Au|Pt|PAn-Cl, and (H) TFE-Pt|Pt|PAn-Cl measured in 0.01 M PBS from -1 V to 1 V at scan rates of 10 mV/s to 100 mV/s in 10 mV/s intervals.

Varying the scan rate of the CV gives further insight into the kinetics of rate controlling processes at the metal polymer interface. **Figure S1** shows cyclic voltammograms for TFE-Au (A), TFE-Pt (B), TFE-Au|Pt (C), TFE-Pt|Pt (D), TFE-Au|PAn-Cl (E), TFE-Pt|PAn-Cl (F), TFE-Au|Pt|PAn-Cl (G), and TFE-Pt|Pt|PAn-Cl (F) measured in 0.01 M PBS from -1 V to 1 V at scan rates of 0.1 V/s, 0.05 V/s, 0.025 V/s, and 0.01 V/s. It is clear that scan rate has little effect of the response of gold in PBS, however the peak shown in TFE-Pt (B) associated with hydrogen evolution shows a response with increasing scan rate. TFE-Au|Pt (C), shows a response similar to TFE-Pt (B) with respect to scan rate. TFE-Au|Pt (C) and TFE-Pt|Pt (D) show quasi-reversible reactions for different values of reduction and oxidation rate constants. TFE-Au|Pt|PAn-Cl (G) exhibits reversible electron processes, as shown in the increasing scan rates. It appears that deposition of PAn-Cl onto an interceding platinum layer via platinization allows for better film adhesion and improved electron transfer kinetics.

| | **Au** | | | **Au\|Pt** | | | **Au\|PAn-Cl** | | | **Au\|Pt\|PAn-Cl** | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | DI | PBS | HEPES | DI | PBS | HEPES | DI | PBS | HEPES | DI | PBS | HEPES |
| $R_s$ (Ω) | 2.52E+03 | 4.85E+01 | 9.30E+02 | 2.00E+03 | 4.41E+01 | 2.15E+03 | 1.30E+03 | 4.23E+01 | 4.68E+02 | 1.23E+03 | 5.10E+01 | 2.41E+03 |
| $Q_{dl}$ (S-sec$^n$) | 3.49E-06 | 1.37E-05 | 7.06E-06 | 4.41E-05 | 2.17E-04 | 7.31E-04 | 1.82E-02 | 1.67E-03 | 2.18E-02 | 1.33E-03 | 1.30E-04 | 1.02E-04 |
| n (0<n<1) | 5.45E-01 | 9.35E-01 | 5.17E-01 | 5.08E-01 | 8.01E-01 | 4.38E-01 | 4.20E-01 | 9.19E-01 | 5.28E-01 | 2.72E-01 | 8.07E-01 | 4.52E-01 |
| $R_{ct}$ (Ω) | 2.72E+04 | 2.81E+06 | 2.85E+04 | 2.09E+03 | 1.79E+04 | 2.15E+03 | 1.42E+03 | 6.15E+01 | 2.88E+01 | 9.95E+03 | 2.30E+04 | 2.61E+03 |
| χ2 | 8.03E-02 | 5.66E-02 | 1.77E-01 | 3.01E-01 | 1.70E-02 | 4.39E-02 | 2.35E-03 | 1.92E-01 | 3.33E-02 | 1.62E-02 | 3.00E-03 | 1.40E-02 |
| | **Pt** | | | **Pt\|Pt** | | | **Pt\|PAn-Cl** | | | **Pt\|Pt\|PAn-Cl** | | |
| | DI | PBS | HEPES | DI | PBS | HEPES | DI | PBS | HEPES | DI | PBS | HEPES |
| $R_s$ (Ω) | 2.52E+03 | 6.94E+01 | 9.40E+02 | 2.21E+03 | 4.09E+01 | 1.16E+03 | 9.48E+02 | 4.90E+01 | 4.92E+02 | 1.28E+03 | 4.42E+01 | 1.23E+03 |
| $Q_{dl}$ (S-sec$^n$) | 5.29E-06 | 1.40E-05 | 1.24E-05 | 4.82E-05 | 2.55E-04 | 8.71E-05 | 6.24E-02 | 1.49E-03 | 2.24E-02 | 1.23E-03 | 2.31E-04 | 1.68E-04 |
| n (0<n<1) | 4.41E-01 | 9.08E-01 | 6.04E-01 | 5.64E-01 | 7.77E-01 | 4.52E-01 | 4.44E-01 | 6.96E-01 | 5.55E-01 | 4.15E-01 | 7.80E-01 | 4.96E-01 |
| $R_{ct}$ (Ω) | 7.13E+04 | 1.76E+06 | 1.53E+04 | 7.29E+03 | 1.88E+04 | 2.40E+04 | 9.38E+01 | 4.96E+01 | 3.90E+01 | 1.34E+04 | 9.57E+04 | 6.15E+04 |
| χ2 | 2.36E-01 | 2.55E-01 | 1.34E-01 | 3.90E-02 | 1.05E-02 | 1.62E-01 | 6.00E-04 | 2.33E-02 | 4.04E-02 | 1.51E-02 | 2.60E-03 | 1.20E-02 |