

Supporting Information

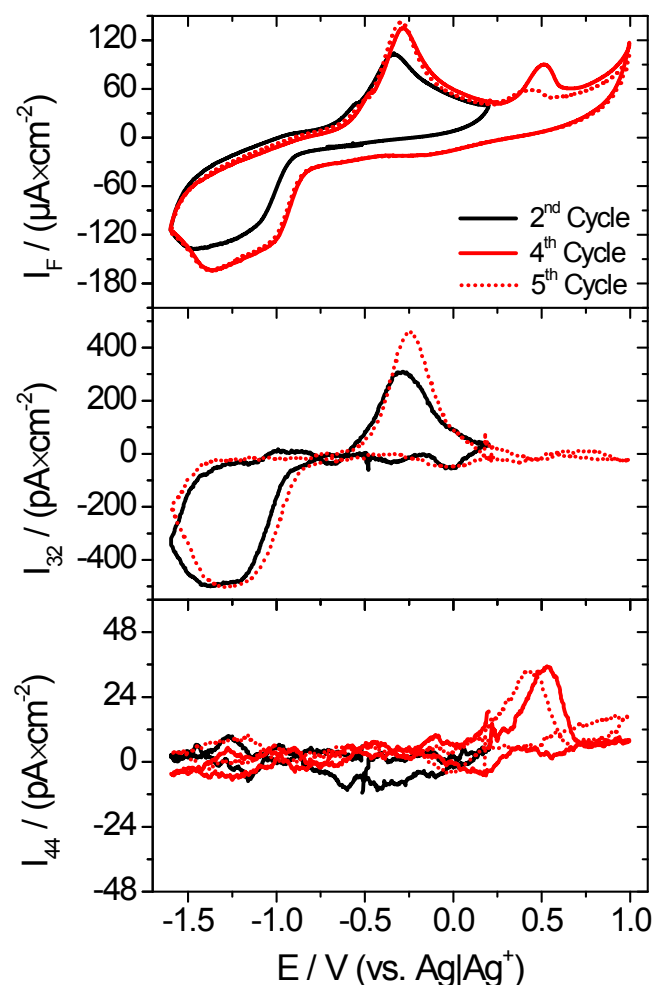


Figure S1: CV (A) and MSCV for mass 32 (B) and mass 44 (C) in an electrolyte of 0.5 M LiClO₄ in DMSO purged with a mixture of argon and oxygen (Ar : O₂ = 80 : 20) at a rhodium electrode (RF = 10.8) decorated with approximately 0.72 ML Se (1 ML is defined as one Se-atom per Rh-surface atom); Sweep rate: 10 mV/s; Flow rate: 5 μL/s. Current densities are given with respect to the geometric surface area.

In the CV of Figure 5A a peak appears at 0.5 V once the upper potential limit was increased from 0.2 V to 1.0 V. This peak is not present in the CV at an unmodified rhodium electrode and disappears in the subsequent sweeps. Therefore the peak is most probably due to the stripping of Se from the rhodium electrode. It is however unclear why Se stripping comes along with the evolution of CO₂. Stripping of Selenium has little affect on the general appearance of the CV and the MSCV for mass 32 in the region of oxygen reduction and oxygen evolution.

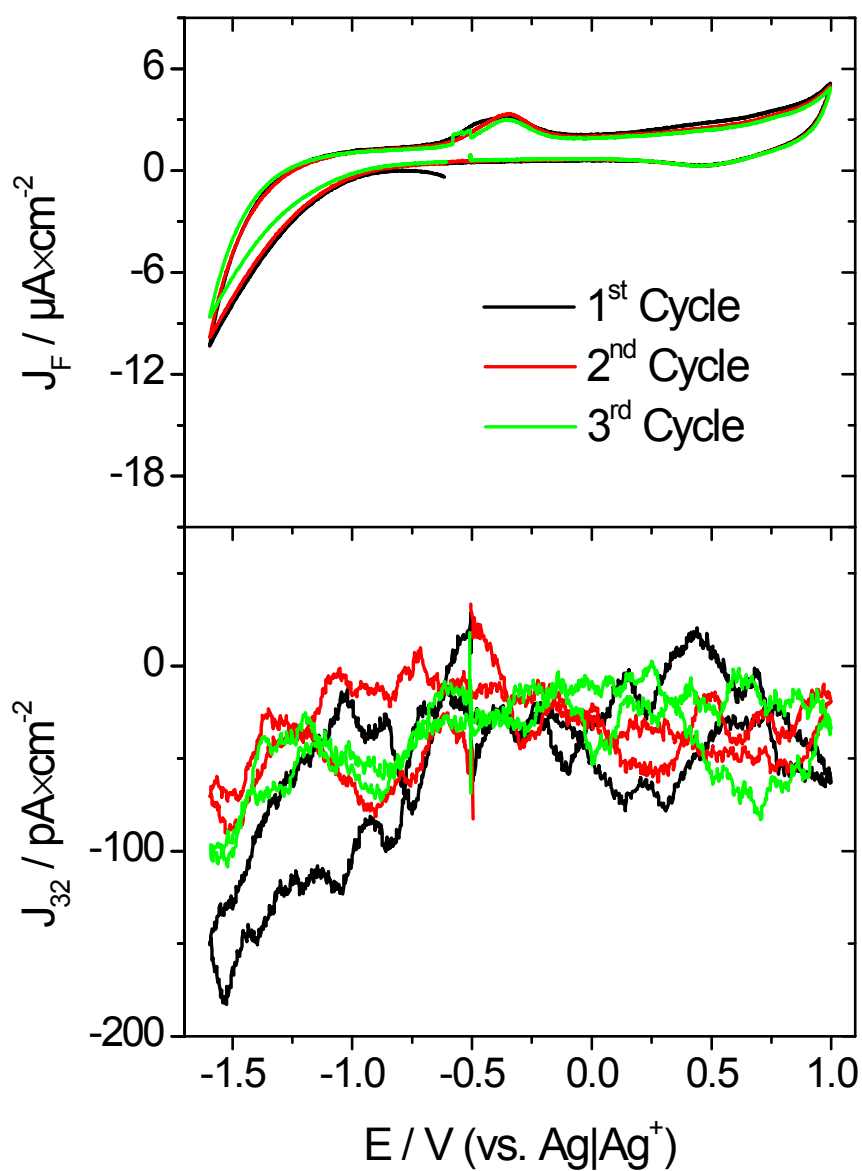


Figure S2: CV and MSCV for mass 32 in an electrolyte of 0.5 M LiClO_4 in DMSO purged with a mixture of argon and oxygen ($\text{Ar} : \text{O}_2 = 80 : 20$); Sweep rate: 10 mV/s; Flow rate: $5 \mu\text{L/s}$; Electrode: BDD_{ox} . All current densities are given with respect to the geometric surface area.

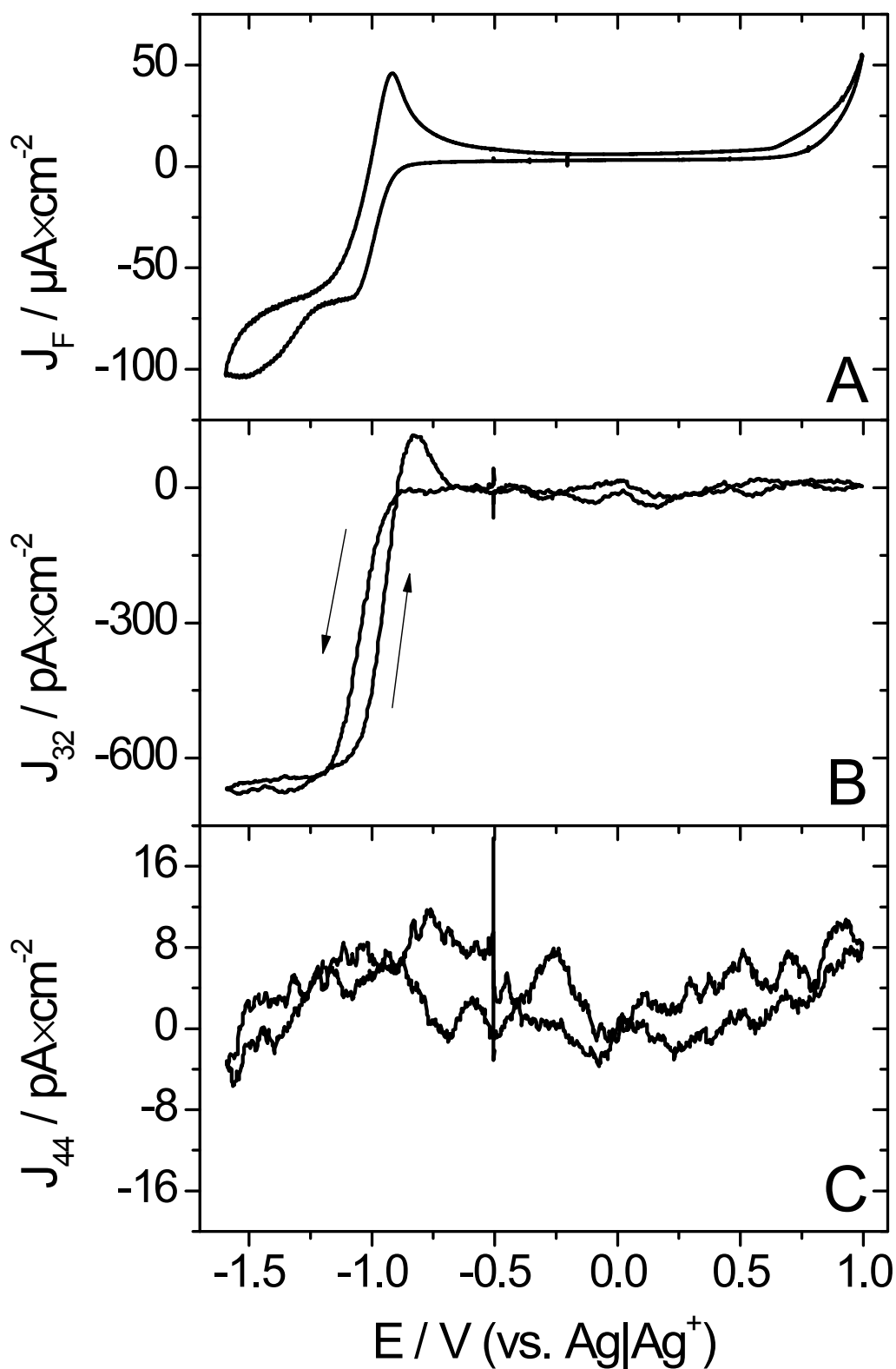


Figure S3: CV (A) and MSCV for mass 32 (B) and mass 44 (C) in an electrolyte of 0.5 M NaClO₄ in DMSO purged with a mixture of argon and oxygen (Ar : O₂ = 80 : 20); Sweep rate: 10 mV/s; Flow rate: 5 μL/s; Electrode: Glassy carbon. All current densities are given with respect to the geometric surface area.

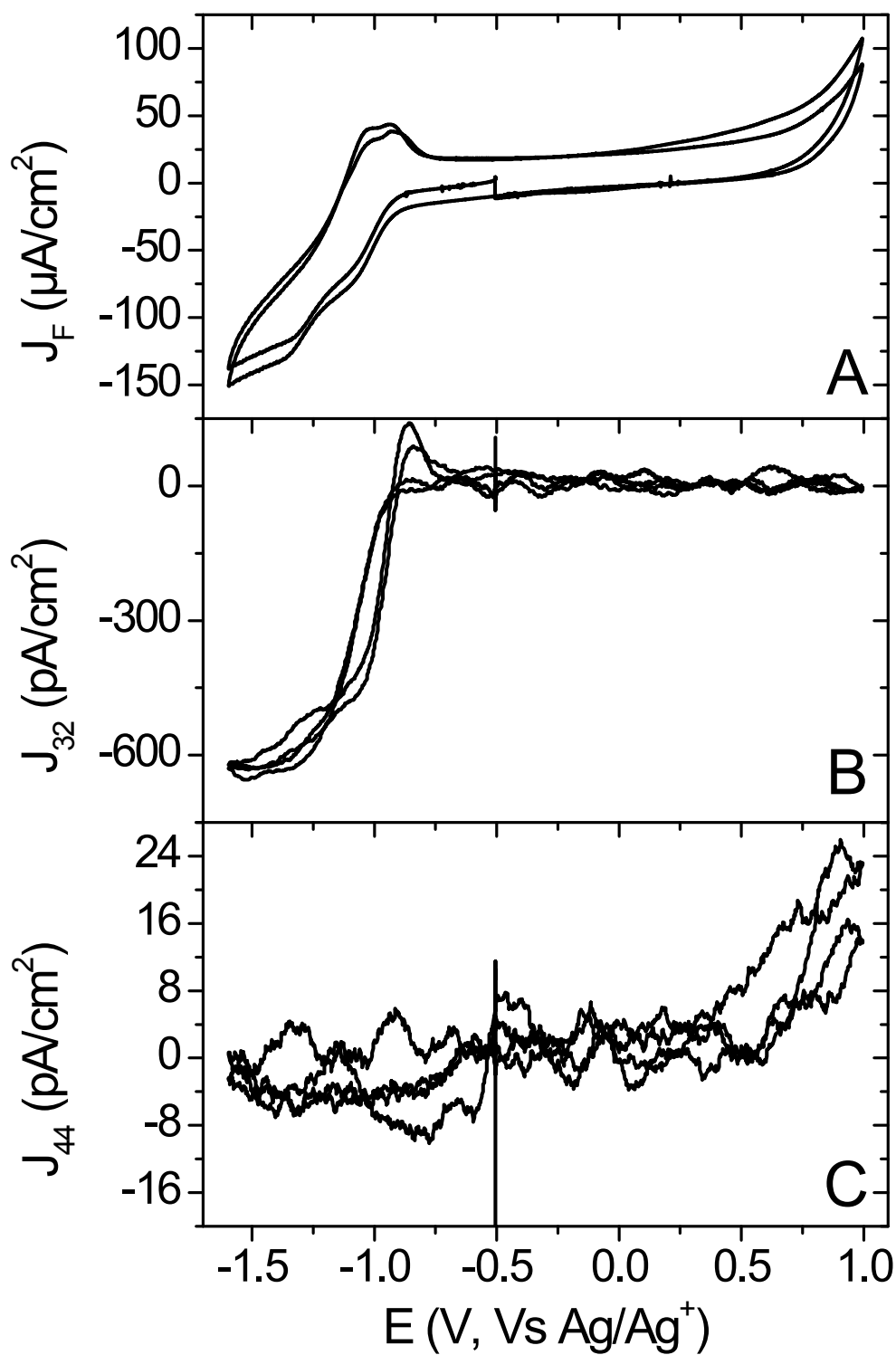


Figure S3: CV (A) and MSCV for mass 32 (B) and mass 44 (C) in an electrolyte of 0.5 M NaClO_4 in DMSO purged with a mixture of argon and oxygen ($\text{Ar} : \text{O}_2 = 80 : 20$); Sweep rate: 10 mV/s; Flow rate: $5 \mu\text{L/s}$; Electrode: Rhodium. All current densities are given with respect to the geometric surface area.

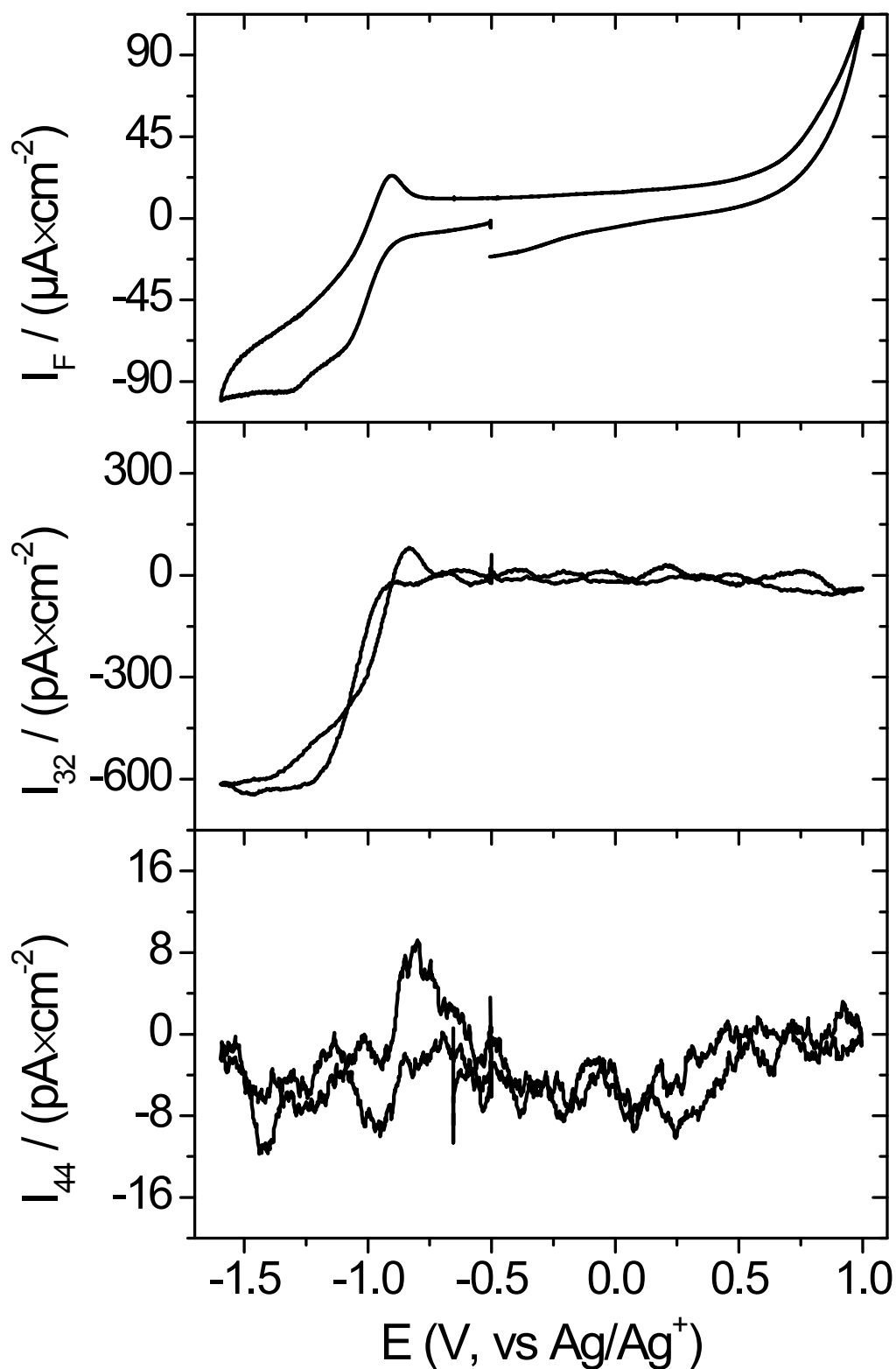


Figure S5: CV (A) and MSCV for mass 32 (B) and mass 44 (C) in an electrolyte of 0.5 M NaClO_4 in DMSO purged with a mixture of argon and oxygen ($\text{Ar} : \text{O}_2 = 80 : 20$); Sweep rate: 10 mV/s; Flow rate: $5\mu\text{L/s}$; Electrode: Ruthenium. All current densities are given with respect to the geometric surface area.

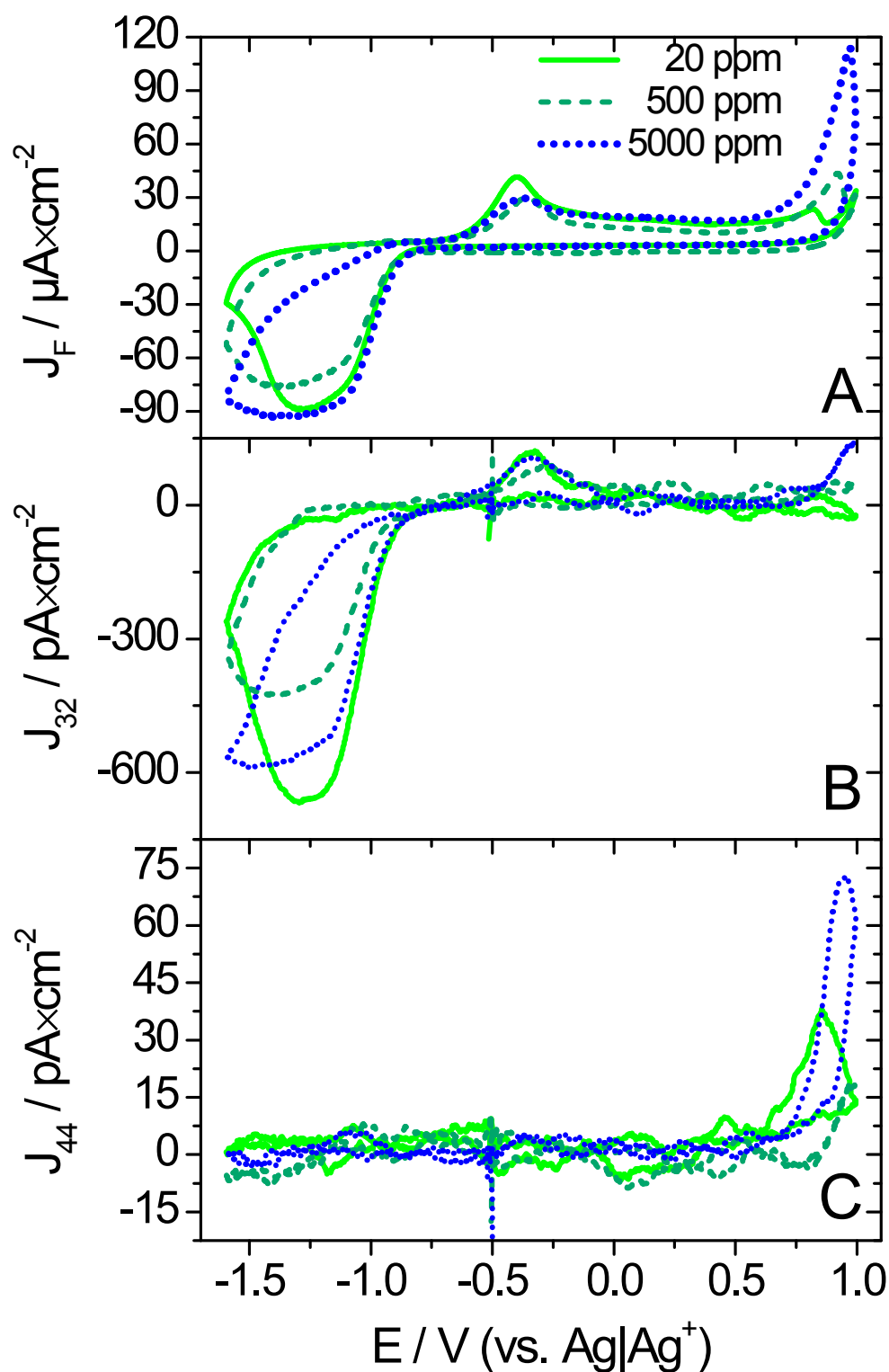


Figure S6: CV (A) and MSCV for mass 32 (B) and mass 44 (C) in an electrolyte of 0.5 M $LiClO_4$ in DMSO with various water contents and purged with a mixture of argon and oxygen ($Ar : O_2 = 80 : 20$); Sweep rate: 10 mV/s;

Flow rate: 5 $\mu L/s$; Electrode: Glassy carbon; Solid 20 ppm water; dashed: 500 ppm water; dotted: 5000 ppm

water. All current densities are given with respect to the geometric surface area.

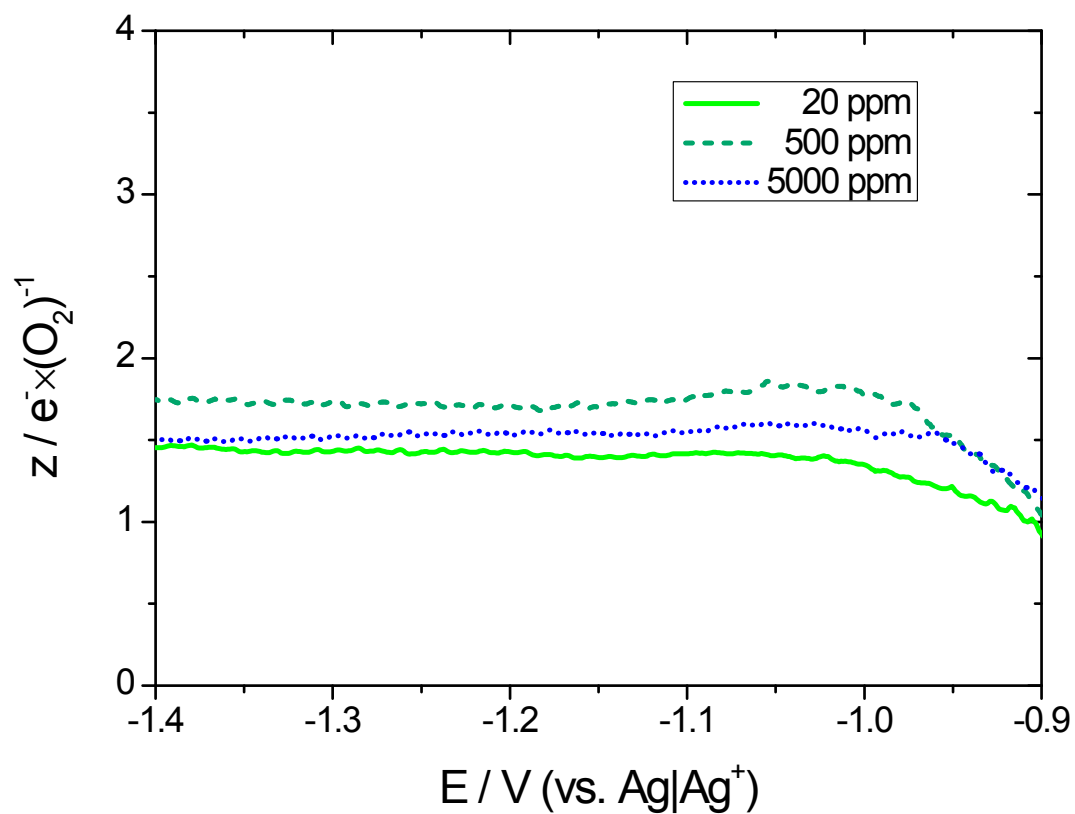


Figure S7: Number of electrons (z) that are transferred per molecule of oxygen in the potential region of oxygen reduction at a glassy carbon electrode in an electrolyte of 0.5 M LiClO₄ in DMSO with various water contents. Solid 20 ppm water; dashed: 500 ppm water; dotted: 5000 ppm water; Sweep rate: 10 mV/s; Flow rate: 5 μ L/s.

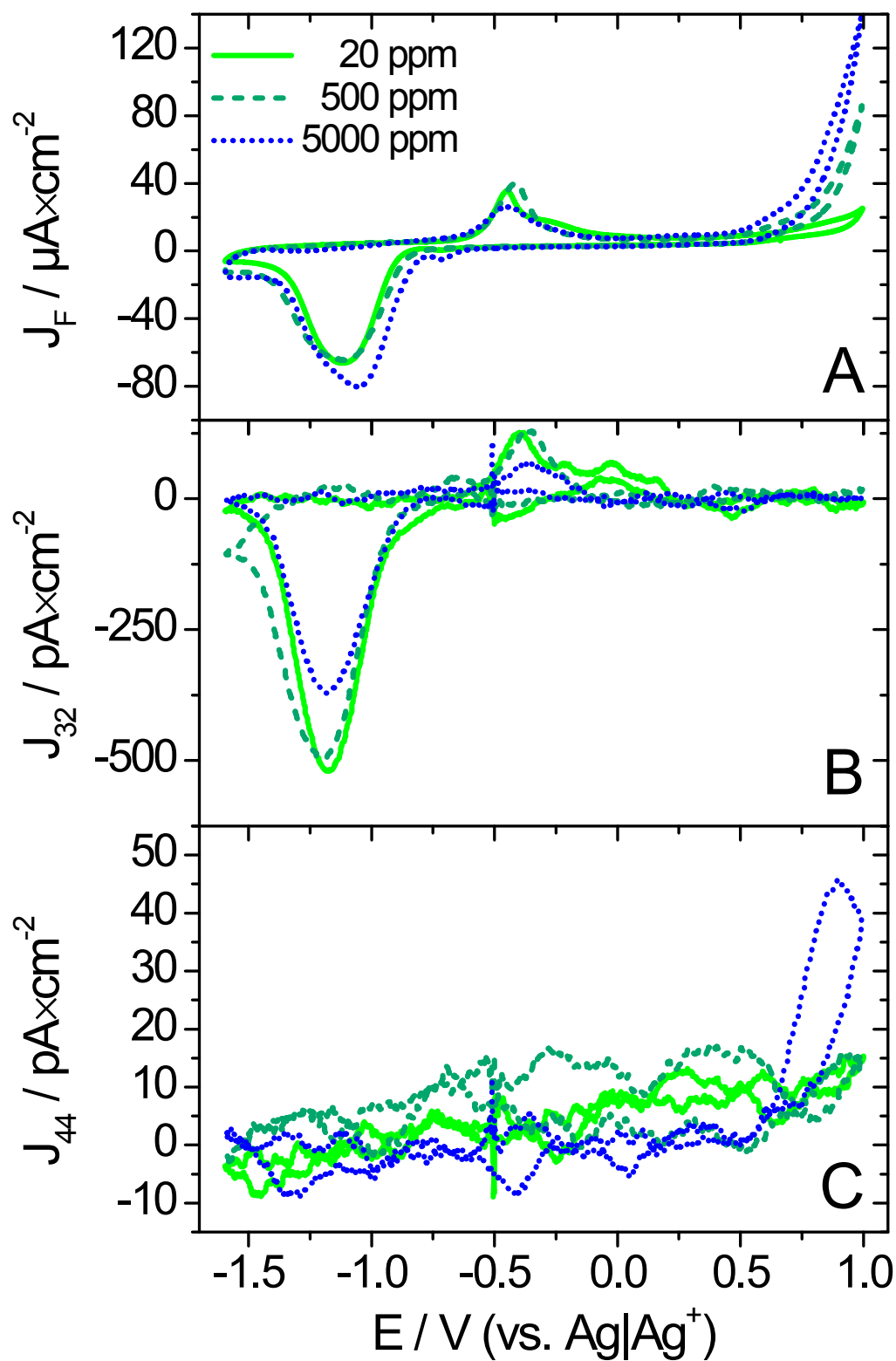


Figure S8: CV (A) and MSCV for mass 32 (B) and mass 44 (C) in an electrolyte of 0.5 M LiClO_4 in DMSO with various water contents and purged with a mixture of argon and oxygen ($\text{Ar} : \text{O}_2 = 80 : 20$); Sweep rate: 10 mV/s; Flow rate: $5\mu\text{L/s}$; Electrode: Pt(pc) ($\text{RF} = 1.4$); Solid 20 ppm water; dashed: 500 ppm water; dotted: 5000 ppm water. All current densities are given with respect to the geometric surface area.

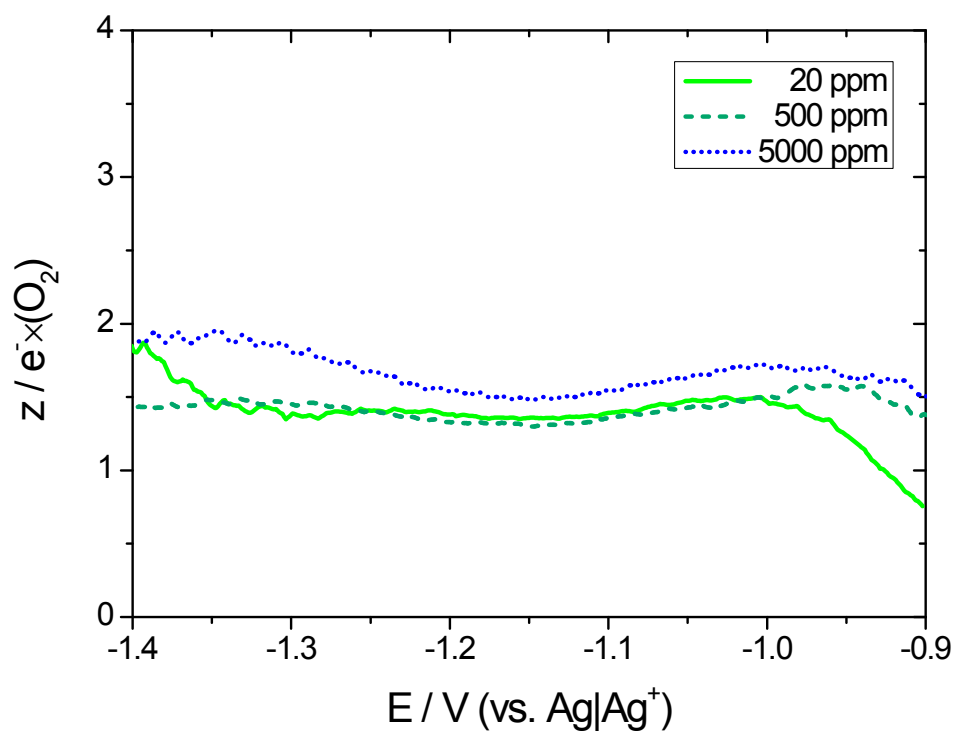


Figure S9: Number of electrons (z) that are transferred per molecule of oxygen in the potential region of oxygen reduction at a polycrystalline platinum electrode in an electrolyte of 0.5 M LiClO₄ in DMSO with various water contents. Solid 20 ppm water; dashed: 500 ppm water; dotted: 5000 ppm water; Sweep rate: 10 mV/s; Flow rate: 5 μ L/s.

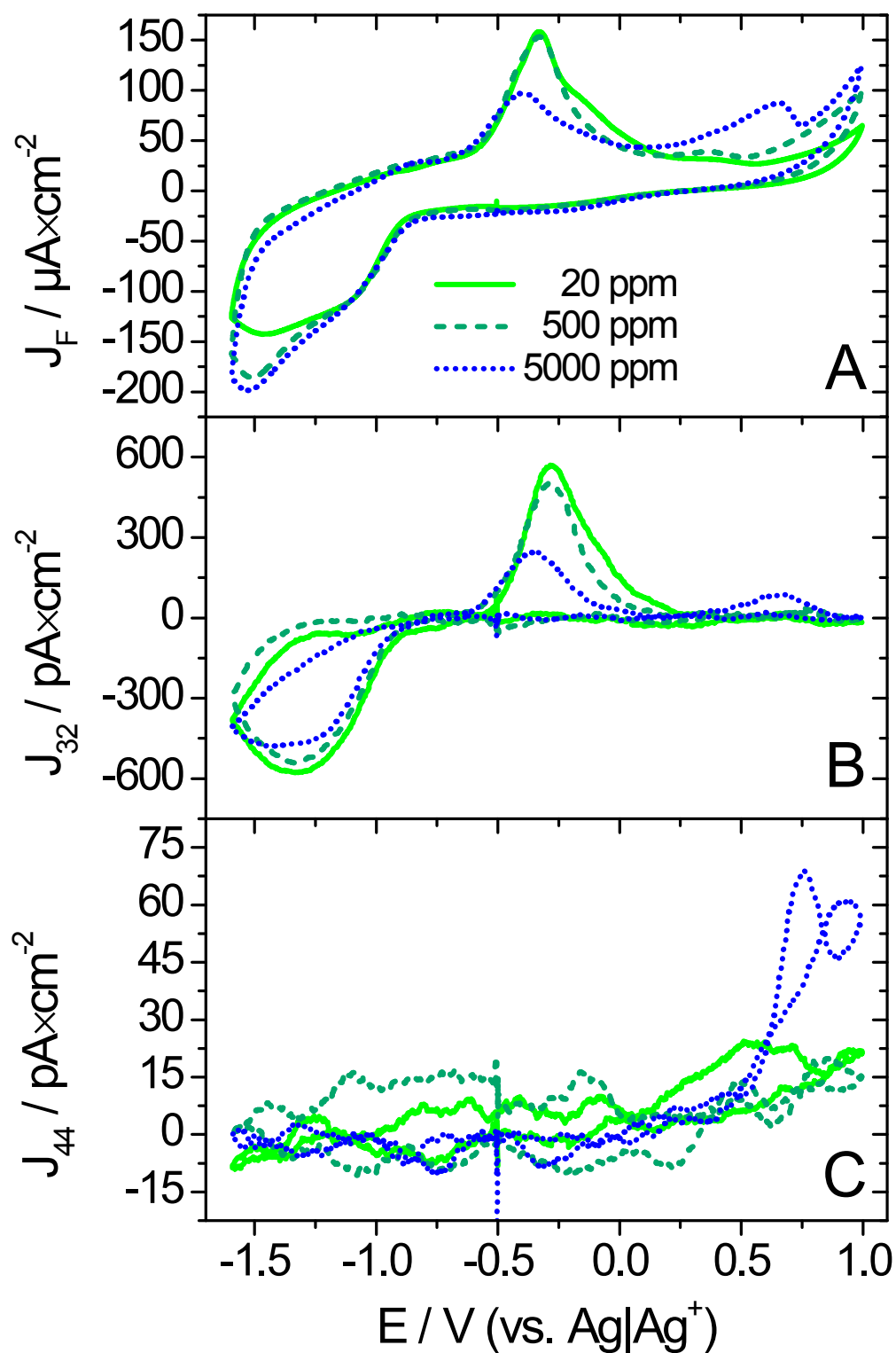


Figure S10: CV (A) and MSCV for mass 32 (B) and mass 44 (C) in an electrolyte of 0.5 M LiClO_4 in DMSO with various water contents and purged with a mixture of argon and oxygen ($\text{Ar} : \text{O}_2 = 80 : 20$); Sweep rate: 10 mV/s; Flow rate: $5\mu\text{L/s}$; Electrode: Rh(pc); Solid 20 ppm water; dashed: 500 ppm water; dotted: 5000 ppm water. All current densities are given with respect to the geometric surface area.

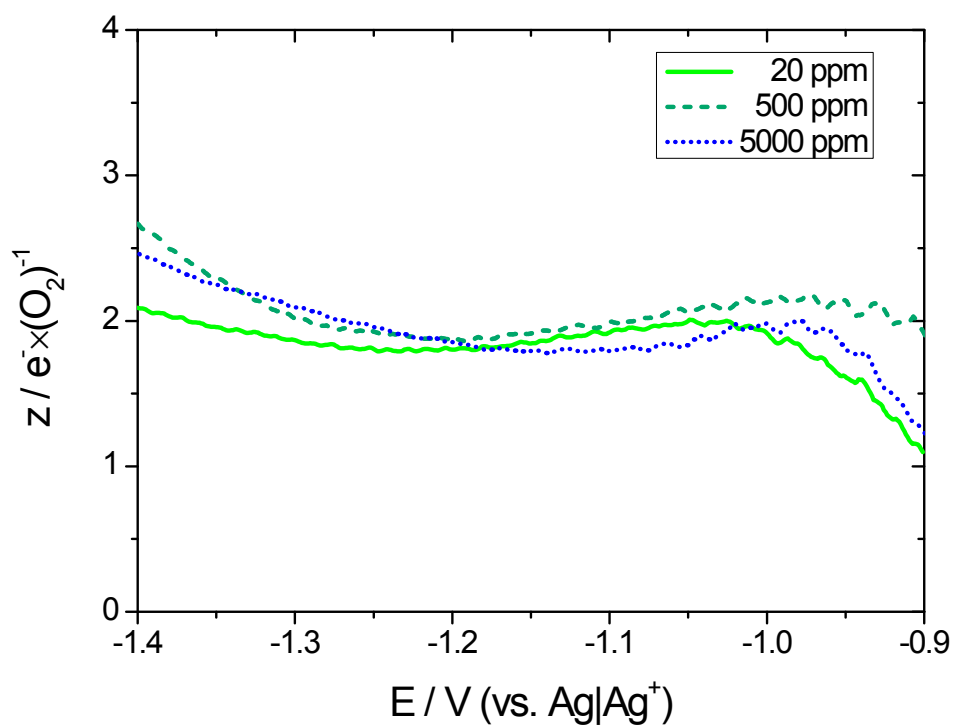


Figure S11: Number of electrons (z) that are transferred per molecule of oxygen in the potential region of oxygen reduction at a polycrystalline rhodium electrode in an electrolyte of 0.5 M LiClO_4 in DMSO with various water contents. Solid 20 ppm water; dashed: 500 ppm water; dotted: 5000 ppm water; Sweep rate: 10 mV/s; Flow rate: 5 $\mu\text{L/s}$.

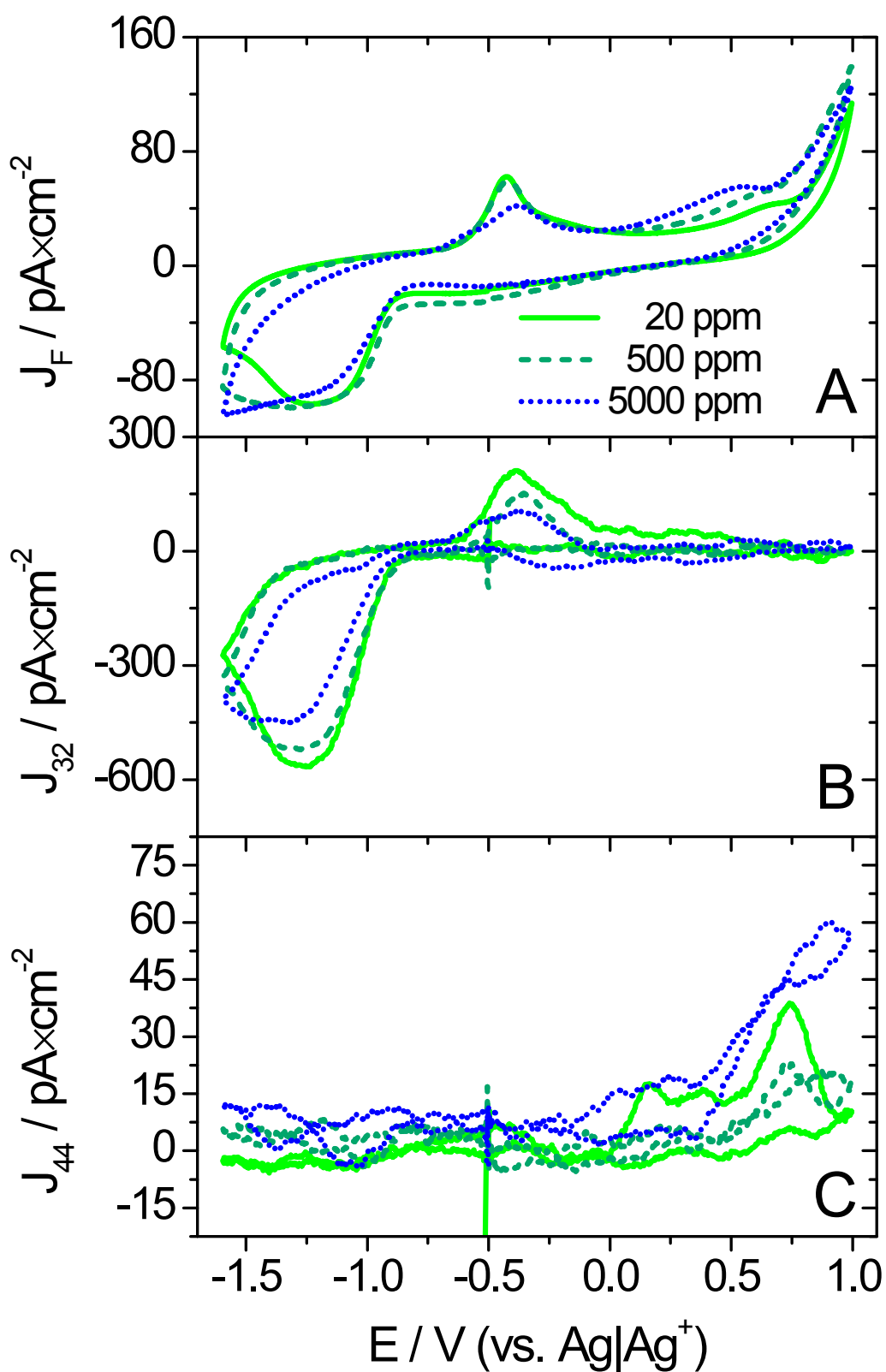


Figure S12: CV (A) and MSCV for mass 32 (B) and mass 44 (C) in an electrolyte of 0.5 M LiClO₄ in DMSO with various water contents and purged with a mixture of argon and oxygen (Ar : O₂ = 80 : 20); Sweep rate: 10 mV/s; Flow rate: 5 μL/s; Electrode: Ru(pc); Solid 20 ppm water; dashed: 500 ppm water; dotted: 5000 ppm water. All current densities are given with respect to the geometric surface area.

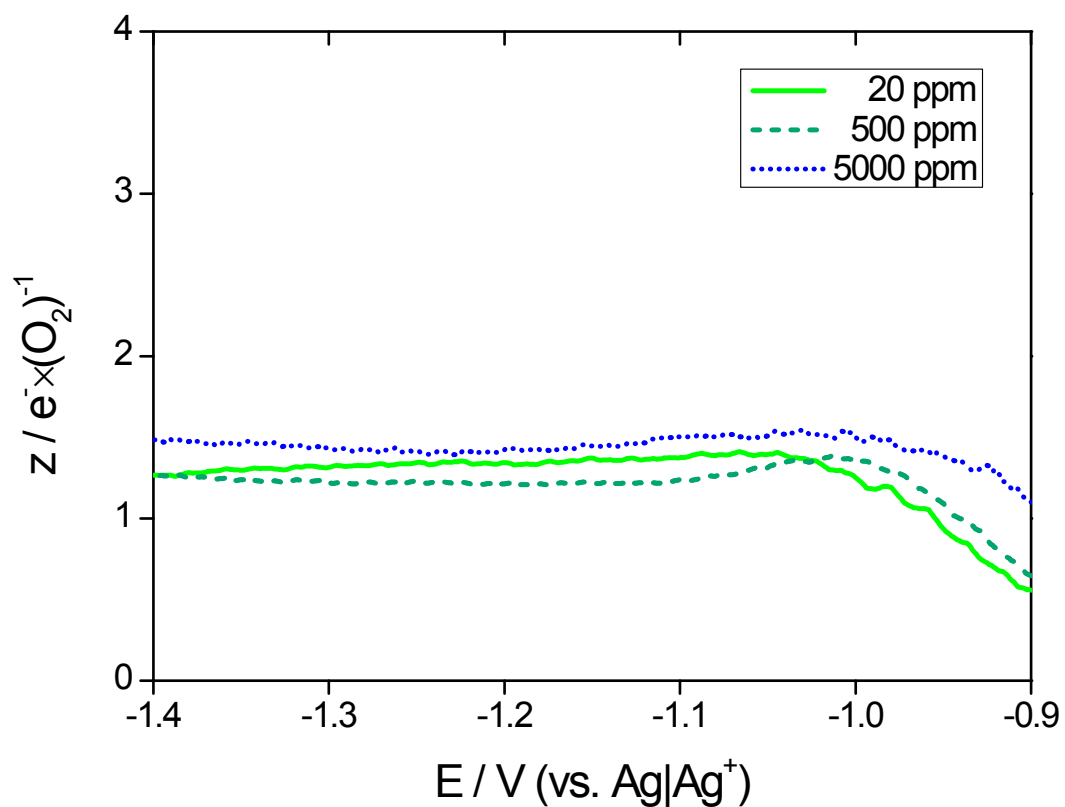


Figure S13: Number of electrons (z) that are transferred per molecule of oxygen in the potential region of oxygen reduction at a polycrystalline ruthenium electrode in an electrolyte of 0.5 M LiClO₄ in DMSO with various water contents. Solid 20 ppm water; dashed: 500 ppm water; dotted: 5000 ppm water; Sweep rate:

10 mV/s; Flow rate: 5 μ L/s.

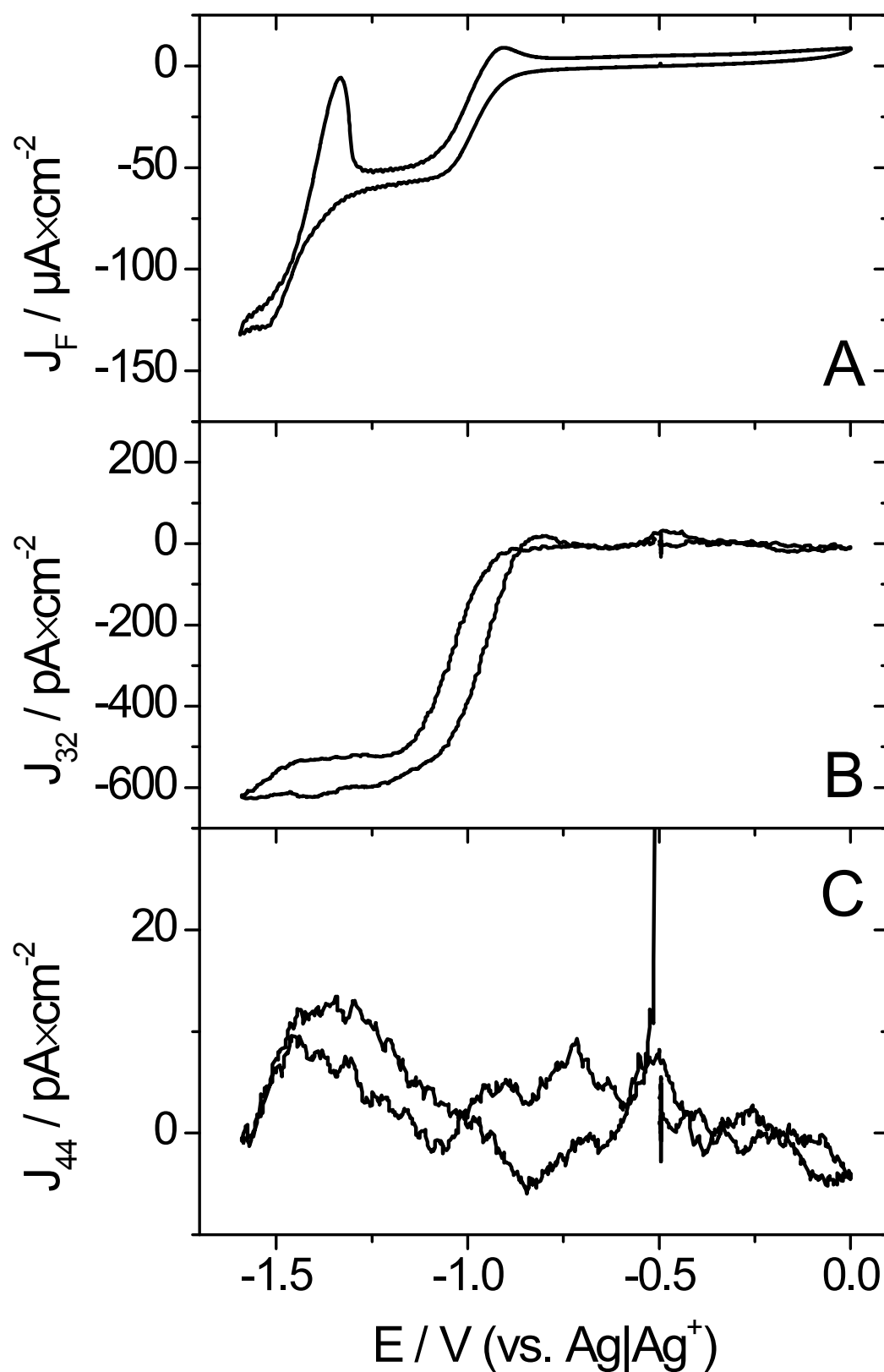


Figure S14: CV (A) and MSCV for mass 32 (B) and mass 44 (C) in an electrolyte of 0.5 M KClO_4 in DMSO purged with a mixture of argon and oxygen ($\text{Ar} : \text{O}_2 = 80 : 20$); Sweep rate: 10 mV/s; Flow rate: $5\mu\text{L/s}$; Electrode: Gold. All current densities are given with respect to the geometric surface area.

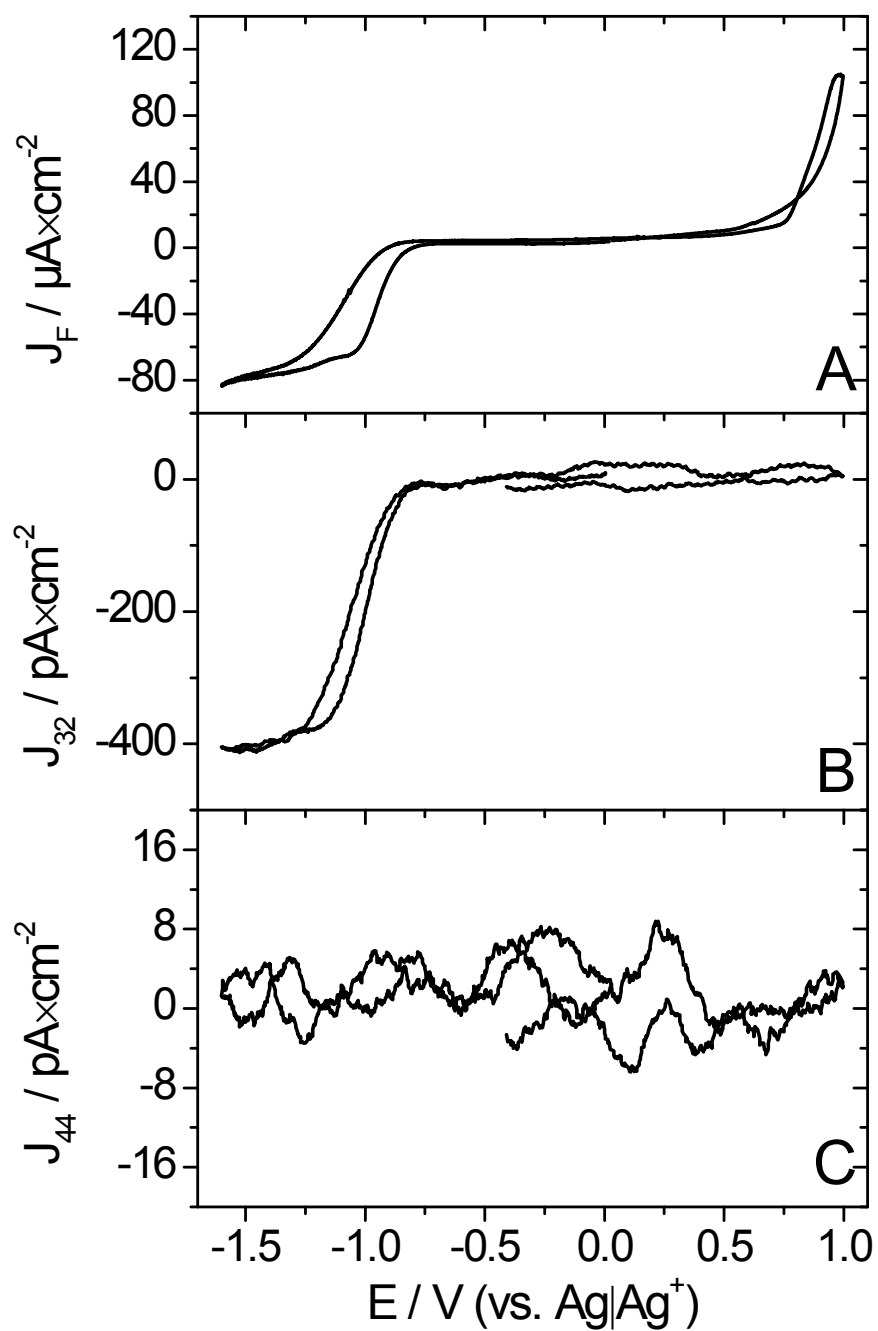


Figure S15: CV (A) and MSCV for mass 32 (B) and mass 44 (C) in an electrolyte of 0.4 M $\text{Mg}(\text{ClO}_4)_2$ in DMSO purged with a mixture of argon and oxygen ($\text{Ar} : \text{O}_2 = 80 : 20$); Sweep rate: 10 mV/s; Flow rate: $5 \mu\text{L/s}$; Electrode: Gold. All current densities are given with respect to the geometric surface area.