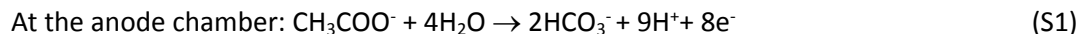


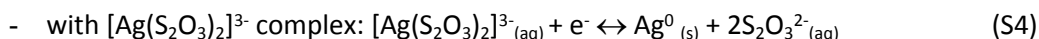
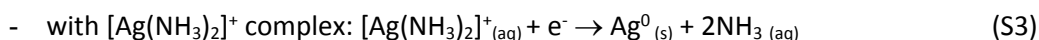
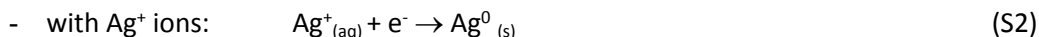
Supplementary data

1. Calculation of electrode redox potential and thermodynamic cell voltages

In BES reactors, the half-cell reactions written in the direction of chemical reduction according to IUPAC convention, are shown in Eq. (S1) and (S2) – (S3) – (S4)



At the cathode chamber:



The thermodynamic anode and cathode potential (E_{an} and E_{ca}) are calculated by the Nernst equation as below.

$$\diamond E_{\text{an}} = E_{\text{an}}^0 - \frac{RT}{nF} \ln \left(\frac{[\text{CH}_3\text{COO}^-]}{[\text{HCO}_3^-]^2 [\text{H}^+]^9} \right) \quad (\text{S5})$$

Where, E_{an}^0 is the electrochemical redox potential at standard conditions (298 K, 1atm, $[\text{H}^+] = 1\text{M}$) ($E_{\text{an}}^0 = +0.187\text{ V}$ versus the Standard Hydrogen Electrode (vs. SHE)), R is the gas constant (8.31447 J/mol/K), T is the absolute temperature (298 K), n is the number of electrons transferred (8 e⁻), F is Faraday's constant (96,485 C/mol), $[\text{H}^+]$ is the concentration of protons in the anolyte (10^{-7} M as pH = 7), $[\text{HCO}_3^-]$ is the concentration of HCO_3^- in the anolyte (5 mM), $[\text{CH}_3\text{COO}^-]$ is the concentration of CH_3COO^- in the anolyte (1.28 g/L, corresponding to COD of 1000 mg/L).

E_{an} was calculated as -0.292 V vs SHE.

$$\diamond E_{\text{ca}} = E_{\text{ca}}^0 - \frac{RT}{nF} \ln \left(\frac{[\text{products}]}{[\text{reactants}]} \right) \quad (\text{S6})$$

$$\begin{aligned} E_{\text{ca}} &= E_{\text{ca}}^0 - \frac{RT}{nF} \ln \left(\frac{1}{[\text{Ag}^+]} \right) \\ \text{- with } \text{Ag}^+ \text{ solution:} \end{aligned} \quad (\text{S6a})$$

$$\begin{aligned} E_{\text{ca}} &= E_{\text{ca}}^0 - \frac{RT}{nF} \ln \left(\frac{[\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} \right) \\ \text{- with } [\text{Ag}(\text{NH}_3)_2]^+ \text{ solution:} \end{aligned} \quad (\text{S6b})$$

$$\begin{aligned} E_{\text{ca}} &= E_{\text{ca}}^0 - \frac{RT}{nF} \ln \left(\frac{[\text{S}_2\text{O}_3^{2-}]^2}{[\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}]} \right) \\ \text{- with } [\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-} \text{ solution:} \end{aligned} \quad (\text{S6c})$$

Where, E_{ca}^0 is the electrochemical cathode potential at standard conditions (298 K, 1atm, $[\text{Ag}] = 1\text{M}$). Depending on type of Ag ions, E_{ca}^0 vs SHE is different (i.e. + 0.799 V for Ag^+ , +0.373 V for $[\text{Ag}(\text{NH}_3)_2]^+$, and + 0.016 V for $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ [1]. At an initial Ag concentration about 10 mM used in the experiments, the E_{ca} accordingly varied. Thus, the thermodynamic cell voltages ($E_{\text{therm}} = E_{\text{ca}} - E_{\text{an}}$) are different and are summarized in Table S1.

Table S1 Electrode redox potential and thermodynamic cell voltages

| Type of Ag(I)-containing solution | Initial Ag(I) concentration | E_{ca}^0 (V) vs SHE | E_{ca} (V) vs SHE | E_{an} (V) vs. SHE | E_{therm} (V) |
|-----------------------------------|-----------------------------|------------------------------|----------------------------|-----------------------------|------------------------|
|-----------------------------------|-----------------------------|------------------------------|----------------------------|-----------------------------|------------------------|

| | | | | | |
|--|------------------------------------|---------|----------|--------|---------|
| Ag^+ | 1000 mg Ag/L \rightarrow 9.26 mM | + 0.799 | + 0.679 | -0.292 | + 0.971 |
| $[\text{Ag}(\text{NH}_3)_2]^+$ | 1000 mg Ag/L \rightarrow 9.26 mM | + 0.373 | + 0.253 | | + 0.545 |
| $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ | 1080 mg Ag/L \rightarrow 10 mM | + 0.016 | + 0.0217 | | + 0.313 |

2. Characterization of electrodeposits at the cathode surfaces

Fig. S1 shows the result of XRD analysis of Ag deposits formed on the cathode surfaces.

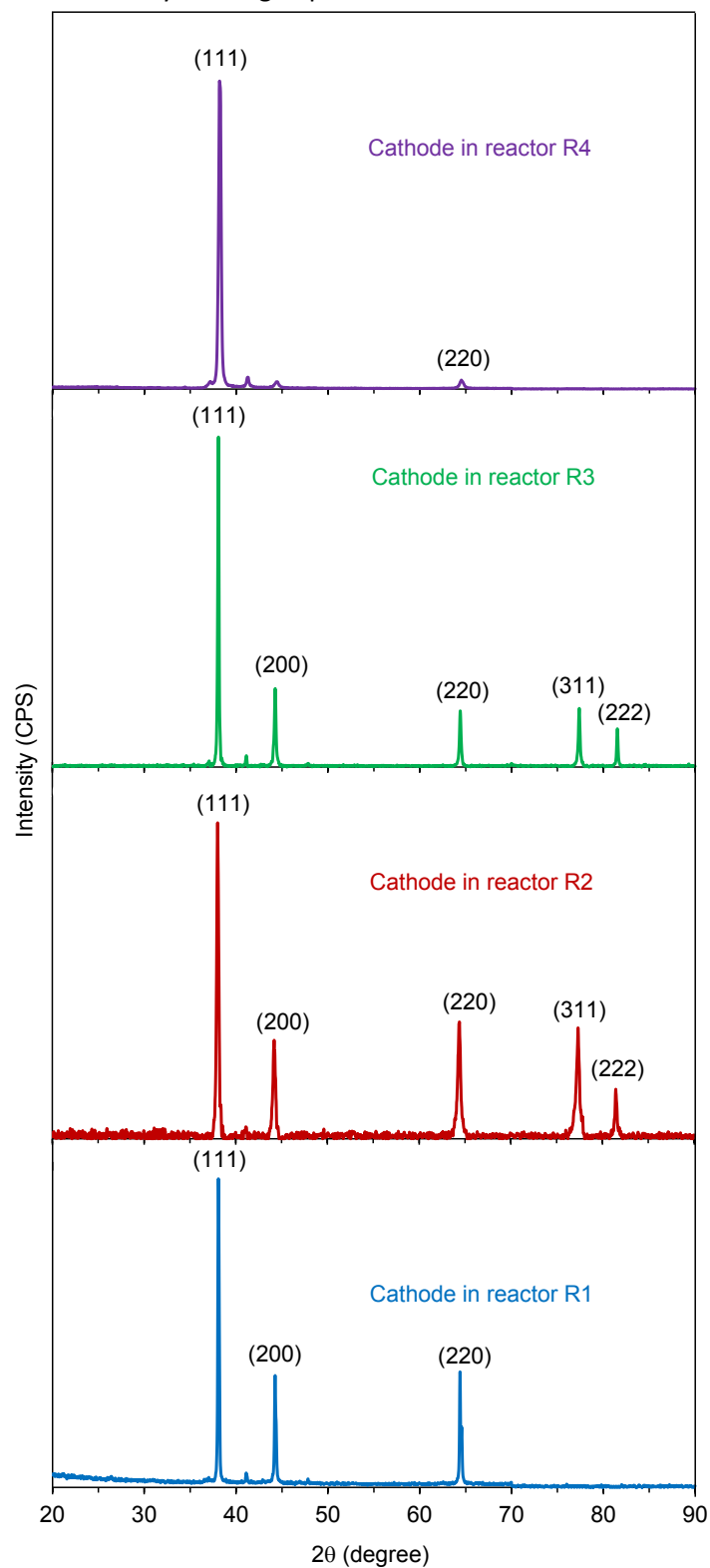


Fig. S1 XRD characterization for confirmation of silver deposits on the cathode surfaces