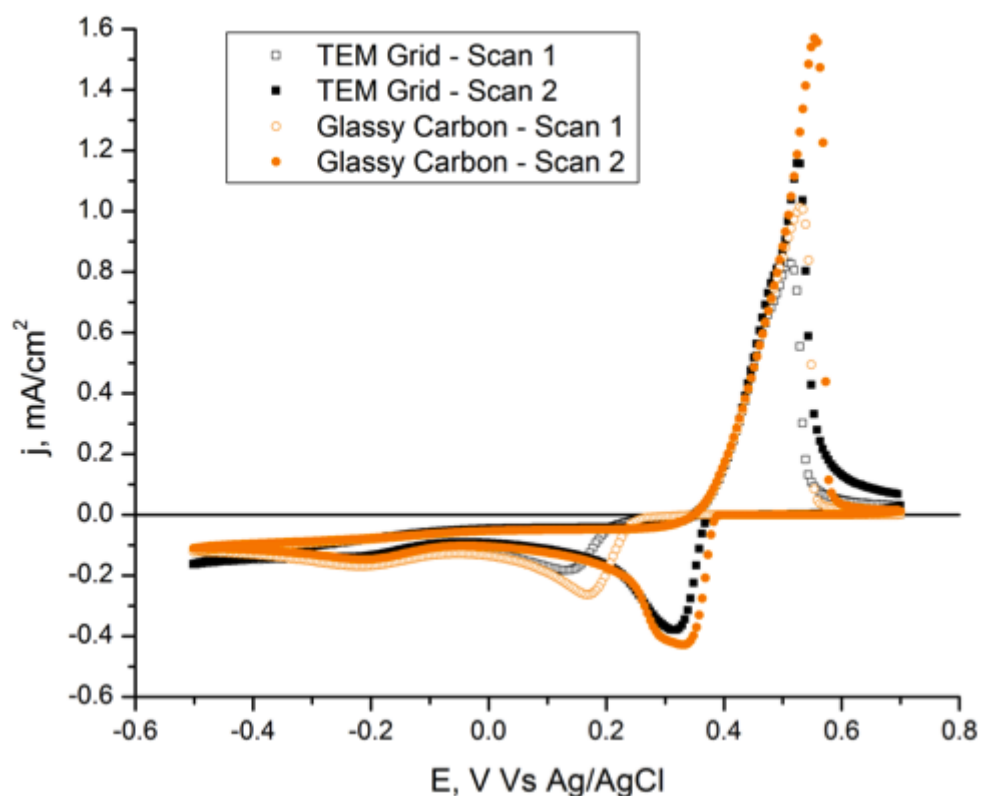


Voltammetry

Potential sweep methods are widely used to study the electrochemical interaction behavior or the reaction mechanism and kinetics of electrochemical systems. A linearly time-varying potential is applied to the working electrode and the current-potential response is recorded. The potential is swept through the potential range where the electrode reactions occur. Besides the potential limits, the direction of the initial sweep and the potential scan rate are important parameters in voltammetry. The main forms of voltammetry are: *linear sweep voltammetry (LSV)* and *cyclic voltammetry (CV)*, when the sweep direction is inverted at a certain potential.

We have used CV for the electrodeposition of silver electrocrystallization on carbonaceous substrates in order to determine the potential range at which the metal can be reduced (electrodeposited) or oxidized (stripped off). In Figure 1, the potential is swept in the cathodic direction starting at the maximum potential. First, the current is zero until the silver reduction onset potential is reached; here the cathodic current increases: the metal is deposited on the substrate. The reduction peak corresponds to zero concentration of silver ion on the electrode surface; and at lower potentials the process becomes diffusion controlled. In the anodic direction, there is a crossover between the anodic and the cathodic curve, which is characteristic of electrodeposition systems. Due to the high lattice mismatch between the metal and the substrate, the metal is deposited on the metal itself and not on the substrate. At more positive potentials the oxidation peak is caused by the stripping of the metal off the substrate.



Cyclic voltammetry of silver electrocrystallization recorded in 1mM AgNO₃ + 0.1M KNO₃ with a glassy carbon and a carbon-coated TEM grid as working electrode (two first scans) [Ustarroz J., Gupta U., Hubin A., Bals S., Terryn H. *Electrochemistry Communications*. 12 (2010) 1706-1709.]