Selenium is an essential trace element in humans, found predominantly in the form of the amino acid, selenocysteine. While it is known that proteins containing selenocysteine in their active site participate in key cellular processes, several questions remain regarding the details of selenium’s physiological redox chemistry. In this work, the voltammetric behavior of the selenocysteine / selenocystine couple on modified gold substrates has been characterized using electrochemical techniques. Known metal-chalcogen reactivity is employed to create ordered and conductive surfaces at which diffusional activity of solution-based selenium analytes can then be recorded. The influences of concentration, holding time, scan rate, and pH on the voltammetric profile are systematically studied and are consistent with a quasi-reversible proton-coupled electron transfer process. The stability and recyclability of the gold-selenium monolayer is examined and a mechanism for the reduction of selenocystine at modified surfaces is proposed.