Towards Understanding the Electrochemical Irreversibility: Origin and Interpretation in Voltammetric Studies

Rubin Gulaboski

Faculty of Medical Sciences, Goce Delcev University, Stip, Macedonia

The concept of *electrochemical irreversibility* originates from the early development of voltammetry, when researchers sought to classify electrode processes according to the speed of the heterogeneous electron transfer. In its strictest sense, irreversibility refers to *sluggish electron transfer kinetics*, or this is the energetic barrier arising when the standard rate constant *ks* is small relative to the characteristic timescale of the voltammetric perturbation. Under such conditions, the current–potential response deviates from the Nernstian equilibrium shape, peak-to-peak separation becomes large, and the backward peak is diminished or absent. This purely kinetic interpretation is formalized within Butler–Volmer and Marcus frameworks, where activation barriers for electron transfer are high.

Yet in practice, many aqueous redox couples that might be expected to behave reversibly show apparent irreversibility. A notable example is the classical transition-metal aquo couple Fe^{3+}/Fe^{2+}:

$Fe^{3+} + 1e^{-} \rightleftharpoons Fe^{2+}$

On purely thermodynamic grounds, the difference in hydration free energies between Fe^{3+} and Fe^{2+} is modest, and their diffusion coefficients are comparable. One might therefore expect facile kinetics and near-reversible cyclic voltammetric responses. However, experimental voltammograms often reveal large peak separations and diminished reverse peaks, hallmarks of irreversibility.

This paradox is explained by recognizing that the *observed irreversibility* is not always due to slow electron transfer. In aqueous solution, Fe^{3+} and Fe^{2+} are rarely present as simple hexaaqua ions; they are subject to hydrolysis and ligand exchange equilibria. For instance, Fe^{3+} can form $FeOH^{2+}$ or more complex hydroxo species, while Fe^{2+} undergoes distinct solvation dynamics. Furthermore, the Fe^{2+} produced at the electrode can be consumed by follow-up chemical reactions (oxidation by dissolved oxygen, disproportionation, or complexation). On the timescale of a voltammetric experiment, these processes may effectively remove Fe^{2+} from the interfacial region, thereby suppressing the backward oxidation wave.

Thus, much of what is termed “electrochemical irreversibility” in real systems is more correctly described as *apparent irreversibility arising from EC or ECE mechanisms*. The electron transfer itself may be intrinsically fast, but the coupled chemistry renders the overall process irreversible on the voltammetric timescale. Distinguishing between these cases requires systematic analysis, such as varying the scan rate, performing digital simulations, or employing complementary spectroscopic techniques.

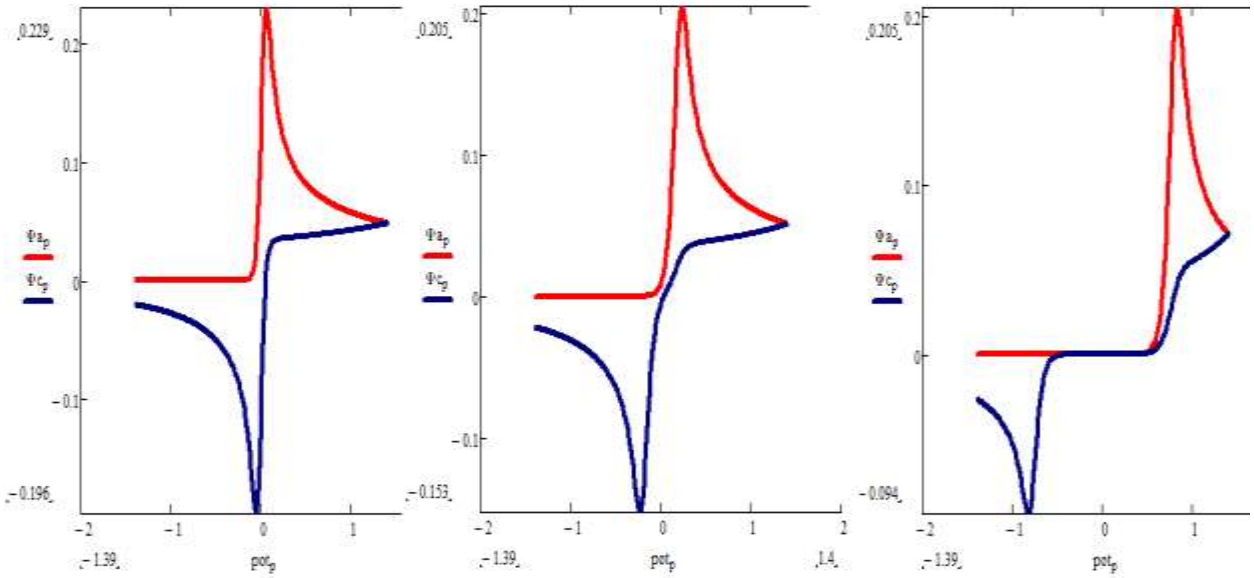
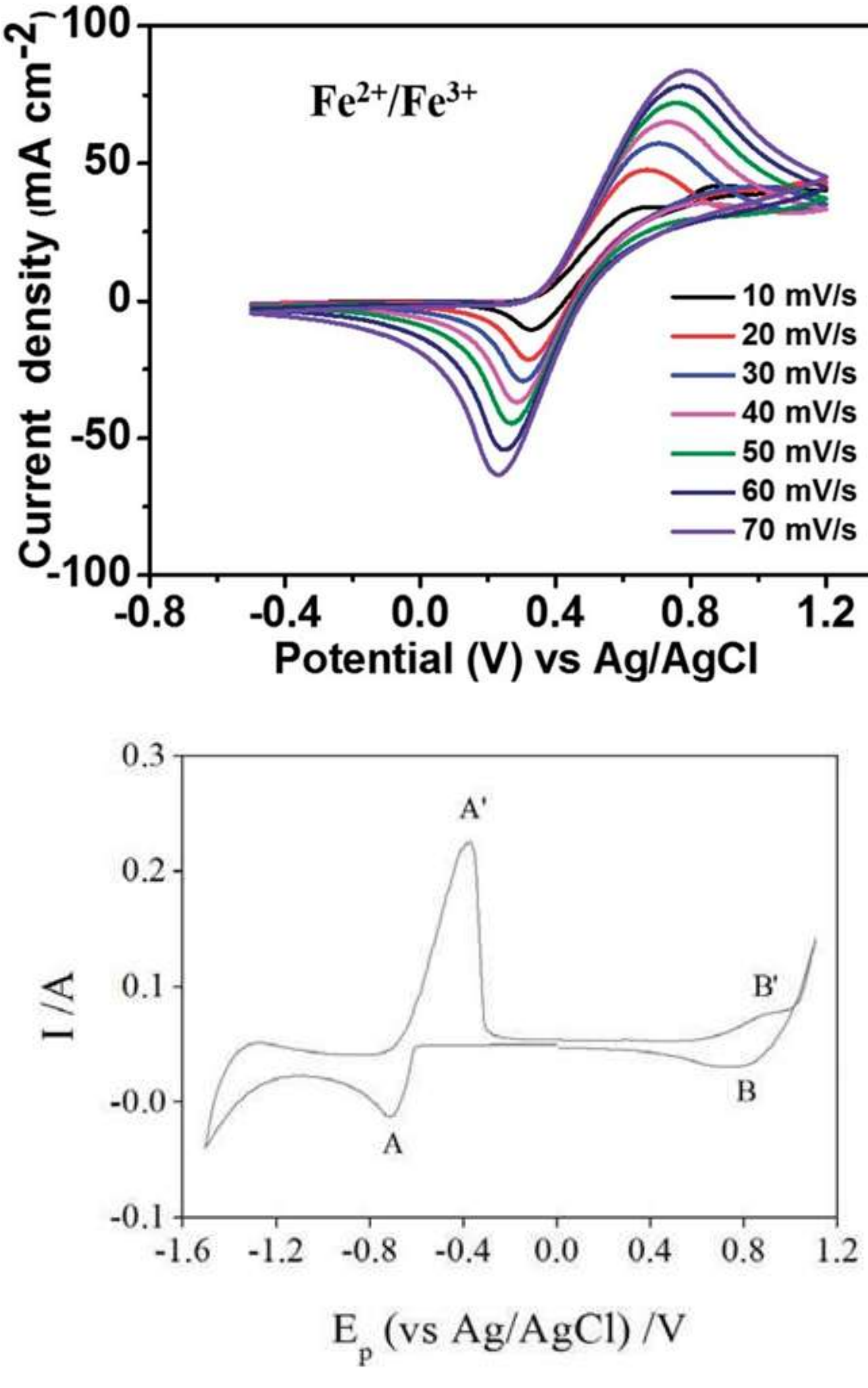


Figure 1. Features of electrochemically reversible (left) quasireversible (middle) and irreversible cyclic voltammograms



Quasireversible and irreversible voltammograms portraying electrode transformation $Fe^{3+} + 1e \rightleftarrows Fe^{2+}$

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