



Electrochemical Cleavage of Alkyl Carbon-Halogen Bonds at Carbon-Metal and Metal-Carbon Substrates: Catalysis and Surface Modification

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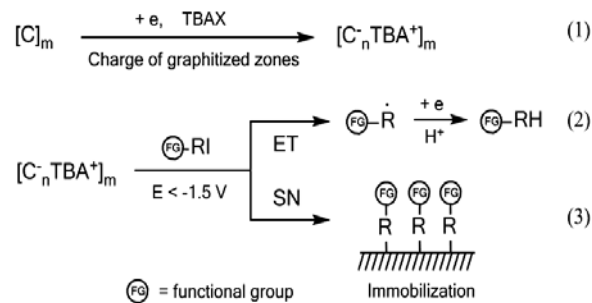
**Cathodic grafting of alkyl chains onto glassy carbon.
Easy immobilization of ferrocene used as redox probe**

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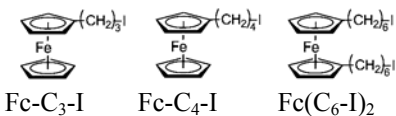
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Primary alkyl iodides (RI, R = Alk with various functional groups non-reducible or reducible at $E < -2$ V) were shown to react with the glassy carbon (GC) surface when it is cathodically charged in aprotic solvents at the potentials more negative than -1.7 V vs. Ag/AgCl. This process corresponds to the cathodic charge of graphitized and fullerenized zones always present in GC [1] followed by a nucleophilic displacement reaction (analogous to an S_N -process in homogeneous chemistry) on alkyl iodides [2]. The reaction thus results in covalent immobilization of the alkyl chains onto carbon.



ω -Iodoalkylferrocenes with different length of the $(CH_2)_n$ spacer have been used as redox probes for this grafting and, for the first time, Fc moieties have been directly attached onto carbon in large amounts to form high-density coverage. In the present work, the immobilization of Fc moiety at a GC surface was achieved using the following precursors:



The large levels of surface coverage with Fc(CH₂)_n groups are explained on the basis of swelling of GC interface provoked by progressive charging of the surface via insertion of tetraalkylammonium cations concomitantly with the target substitution process.

All primary alkyl iodides C_nH_{2n+1}I (with $n > 3$) exhibit similar behavior (fig. 1). Alkyl ferrocene layers attached to GC are chemically and electrochemically stable. The levels of surface coverage obtained by this method are high (fig. 2), reaching the apparent surface concentrations of 8×10^{-9} mol cm⁻². Such large levels of the coverage with Fc(CH₂)_n groups are explained by swelling of GC interface provoked by progressive charging of the surface via insertion of tetraalkyl ammonium cations [3] concomitantly with the target substitution process.

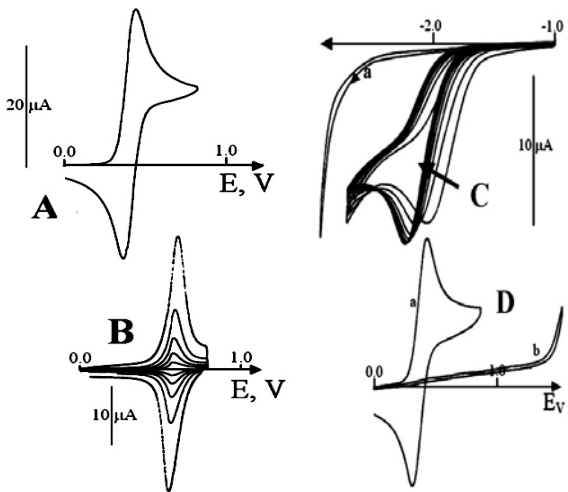


Fig. 1. Voltammetry at GC electrode (0.8 mm²) in AN+TBABF₄. A: Oxidation of 3-Iodopropylferrocene (17 mM) at a GC electrode. $\nu = 50$ mV s⁻¹. B: Response (at $\nu = 20 \dots 500$ mV s⁻¹) of the cathodic deposit obtained after a 30s hold at -2.4 V. Surface density of Fc-C₃H₆ moieties from current integration: 8.2×10^{-9} mol cm⁻². C: 1-Iodo-octane (6.5 mmol L⁻¹) in DMF + TBABF₄. First eight scans (a shows the baseline). D: (a)—Response of the solution of K₄[Fe(CN)₆] in saturated aqueous KCl at a bare GC electrode; (a)— same solution at the modified GC electrode.

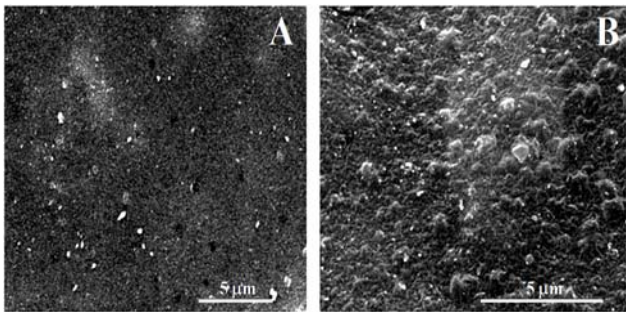


Fig. 2. SEM images of GC electrode surfaces before and after electrochemical reduction. DMF + 0.1M TBABF₄. (A)—Initial GC surface. (B)—Blank experiment on the same GC sample with a hold of potential at -2.5 V during 5 min.

References

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