

# SIMULTANEOUS ELECTROGRAFTING OF ORGANIC LAYERS WITH DIFFERENT FUNCTIONALITIES ON CARBON ELECTRODES

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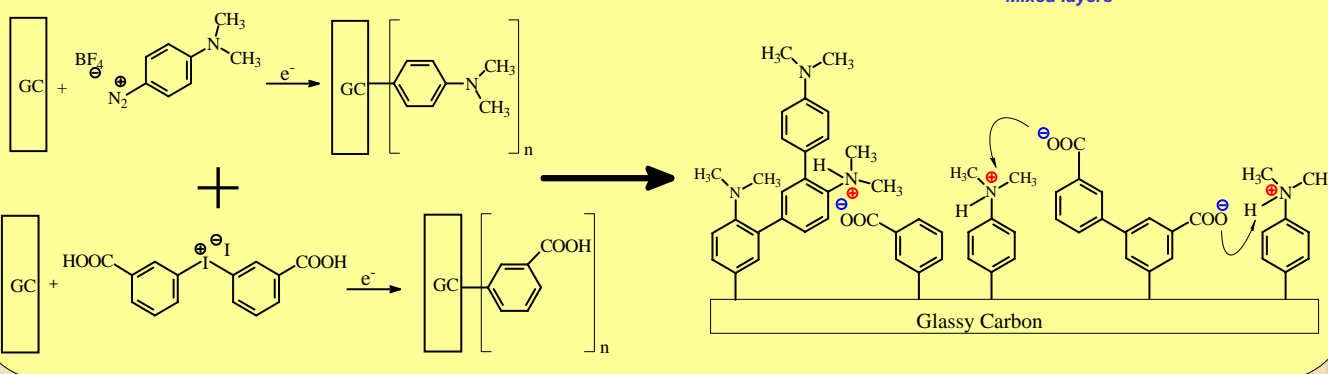
**Motivation for the work:** Derivatization of carbon surfaces is an important tool in the design of new functional materials. The most widely employed electrochemical procedures for derivatizing carbon surfaces consist of the electrochemical oxidation of amines and alcohols or the electrochemical reduction of aryldiazonium and iodonium salts. The modification procedures involve the electrogeneration of reactive radicals in the vicinity of the carbon surface, leading to the formation of covalent linkages with the surface. With these reductive methods, the surfaces are not roughened and sub-monolayer, monolayer, or multilayer coverages can be obtained. Applications have been reported in fields as diverse as material chemistry, electrocatalysis, combinatorial chemistry and analytical sensors.

The covalently attached organic groups impart different properties to carbon surfaces. We set out to look for answers to a few fundamental questions which have been hitherto not investigated.

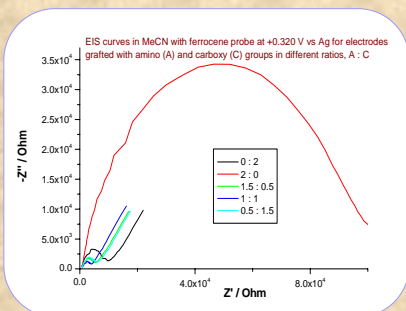
Is it possible to simultaneously attach two different functional groups from two different classes of precursors in a single electrolysis step?  
Is it possible to vary the ratios of each functional group on the surface?  
How do the surface properties vary with the different ratios of organic functional groups?

**Procedure:** Glassy carbon electrodes were grafted with dimethyl amino and / or carboxylic groups from acetonitrile solutions of N, N-dimethylaminophenyldiazonium tetrafluoroborate and 3,3'-dicarboxyphenyliodonium iodide in different ratios by cyclic voltammetry and potentiostatic electrolysis. Analysis of the electrodes after grafting and ultrasonication in MeCN was performed in MeCN with ferrocene as probe and in aqueous media of pH ~ 1 (0.1 M KCl + HCl) and pH ~ 7.5 (0.2 M KCl) with  $K_3Fe(CN)_6$  as the redox probe. Electrochemical Impedance Spectroscopy (EIS) was carried out on the grafted and bare electrodes at the respective  $E^0$  values of ferrocene and ferricyanide probes over the range of 0.1 – 100000 Hz with a 5 mV imposed AC signal.

## Electrografting via electro-reduction of diazonium and iodonium salts

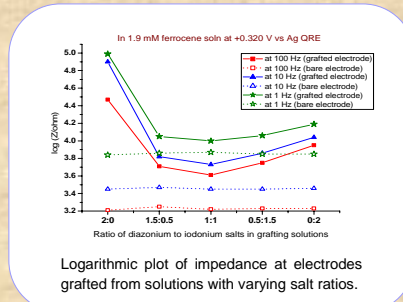


## Mixed layers



With the ferrocene probe in acetonitrile, the impedance values are nearly constant for each of the 5 bare electrodes at the 3 frequencies. After grafting, the same electrodes exhibit higher impedances at all ratios and frequencies but they all present a minimum when the ratio of salts in grafting solutions is 1:1.

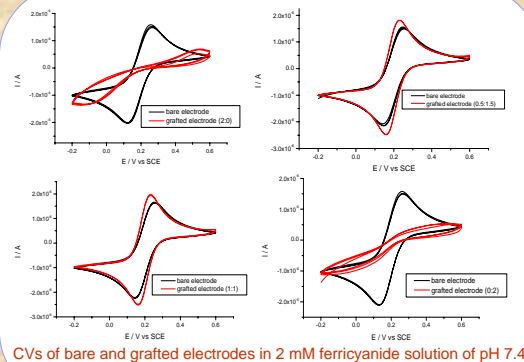
This implies that mixed layers containing both amino and carboxy groups are formed on the electrode surfaces grafted from mixed solutions. The presence of both acidic and basic groups immobilized on a surface in close proximity allows for charge transfer to occur and make the layer less impervious. (Please note that the impedance values for pure amino or pure carboxy layers are much higher than for mixed layers; with the pure amino layer having the largest blocking effect).



A similar trend is found in aqueous media with ferricyanide as probe. More interestingly we see a reversal of behaviour when the electrodes are grafted with mixed layers.

Cyclic Voltammetry curves reveal that the redox process of ferricyanide is hindered at electrodes with pure amino or carboxy layers, whereas it seems to be "enhanced" at electrodes with mixed layers.

Ferricyanide has a lower heterogeneous rate constant compared to ferrocene; and some impedance is presented even at bare electrodes. But when coated with a mixed layer permitting charge transfer, the impedance is reduced.

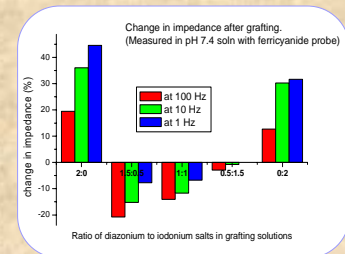


CVs of bare and grafted electrodes in 2 mM ferricyanide solution of pH 7.4

Ferrocene has a very high rate constant; hence the charge transfer resistance is insignificant at the bare electrodes. Therefore the reversal phenomenon is not observed with such probes.

With the ferricyanide probe, reversal of impedance behaviour on grafting with mixed layers is observed both in acidic as well as slightly alkaline media when either the amino or the carboxy groups are charged due to protonation / deprotonation.

In acetonitrile and in aqueous media of pH ~7.5, the pure amino layer had the largest impedance, but in aqueous medium of pH 1.1, the pure carboxy layer had the highest impedance.

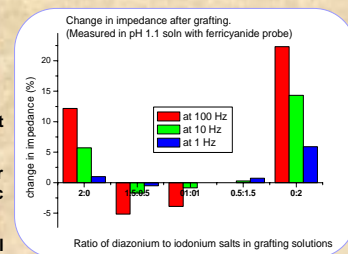


## CONCLUSIONS AND FUTURE OUTLOOK

Cyclic voltammetry and Impedance analysis reveal that it is possible to graft conducting surfaces with mixed layers from different kinds of precursors.

A mixed layer with complementary functional groups leads to charge transfer phenomenon within the layer. This property can be exploited for organic molecular electronics.

More surface studies need to be done to ascertain if the ratio of the functional groups on the surface is same as in the solutions from which they are grafted.



## References

- 1) P. Allongue, M. Delamar, B. Desbat, O. Fagebaume, R. Hitmi, J. Pinson, and J. -M. Saveant, *J. Am. Chem. Soc.*, 119 (1997) 201- 207.
- 2) K. H. Vase, A. H. Holm, K. Norrman, S. U. Pedersen, and K. Daasbjerg, *Langmuir.*, 23 (2007) 3786 – 3793.