



# Enhancing charge storage of conjugated polymer electrodes with phenolic acids



Michal Wagner, Tomasz Rębiś, Olle Inganäs\*

*Biomolecular and Organic Electronics, IFM, Linköping University, S-581 83 Linköping, Sweden*

## HIGHLIGHTS

- Synthesis of conjugated polymer with outstanding electrochemical stability.
- Doping of electrochemically stable electrodes with phenolic acids.
- Significant enhancement in electrodes capacitance upon doping was achieved.
- Fast electron transfer for hydroquinone/quinone conversion was observed.

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## ABSTRACT

We here present studies of electrochemical doping of poly(1-aminoanthraquinone) (PAAQ) films with three structurally different phenolic acids. The examined phenolic acids (sinapic, ferulic and syringic acid) were selected due to their resemblance to redox active groups, which can be found in lignin. The outstanding electrochemical stability of PAAQ films synthesized for this work enabled extensive cycling of phenolic acid-doped PAAQ films. Potentiodynamic and charge–discharge studies revealed that phenolic acid-doped PAAQ films exhibited enhanced capacitance in comparison to undoped PAAQ films, together with appearance of redox activity characteristics specific for each dopant. Electrochemical kinetic studies performed on microelectrodes affirmed the fast electron transfer for hydroquinone-to-quinone reactions with these phenolic compounds. These results imply the potential application of phenolic acids in cheap and degradable energy storage devices.

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## 1. Introduction

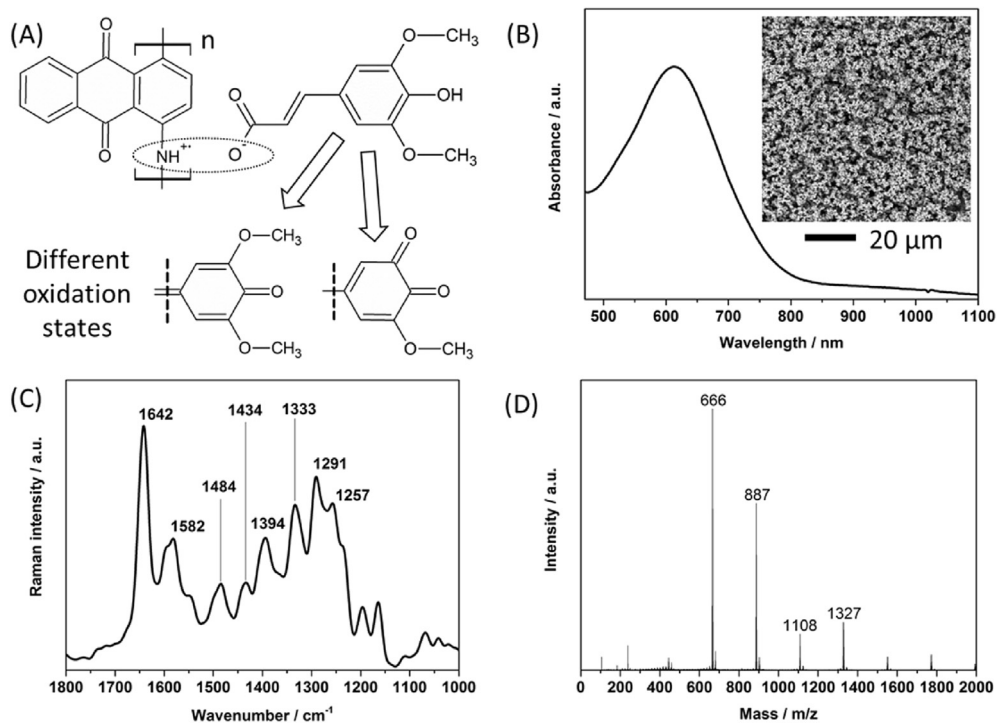
The electrochemistry of quinones has been extensively studied in the past, due to the role of quinones in bioenergetics [1–3]. Hydroquinone-to-quinone conversion, can be used for e.g. effective charge storage [4,5] or in electrochemical sensing [6,7]. Quinones can theoretically provide significant values of specific capacity, competitive even with lithium ion-based systems [8]. Due to the intermittency of electricity supply from solar and wind energy, there is a need of cost-effective energy storage systems. This must be based on cheap and abundant energy materials. Phenolic-type compounds are abundant in nature, ranging from e.g. humic acid to flavonoids and lignins. Therefore it is attractive to use phenolics derived from natural sources. Lignin, one of the two major structural components of wood, a whole class of polymeric materials

rich in phenols, could be a practical choice. It was already shown that lignin can be used directly in energy storage [9] or in electrochemical sensing [10] when combined with conjugated polymers, which then acts as a current collector for redox active groups. The limits to use of lignin in this context may be studied with the help of isolated redox active building blocks of lignin. These are the sinapyl, coniferyl, and para-coumaryl alcohols, which are used by plants for oxidative polymerization of lignin [11]. In the present work we selected three structurally different monolignol-like compounds in their acidic form (see inserts in Fig. 3A, B and C). The phenolic acids (sinapic, ferulic and syringic) resemble two redox active groups in lignin and differ by the number of methoxy groups as well as the length of side chain in para-position. With these compounds as models for the smallest elements of lignins, we may study the redox conversion of monolignols, thus approaching a study of the upper limits for charge storage to be found with lignin derivatives.

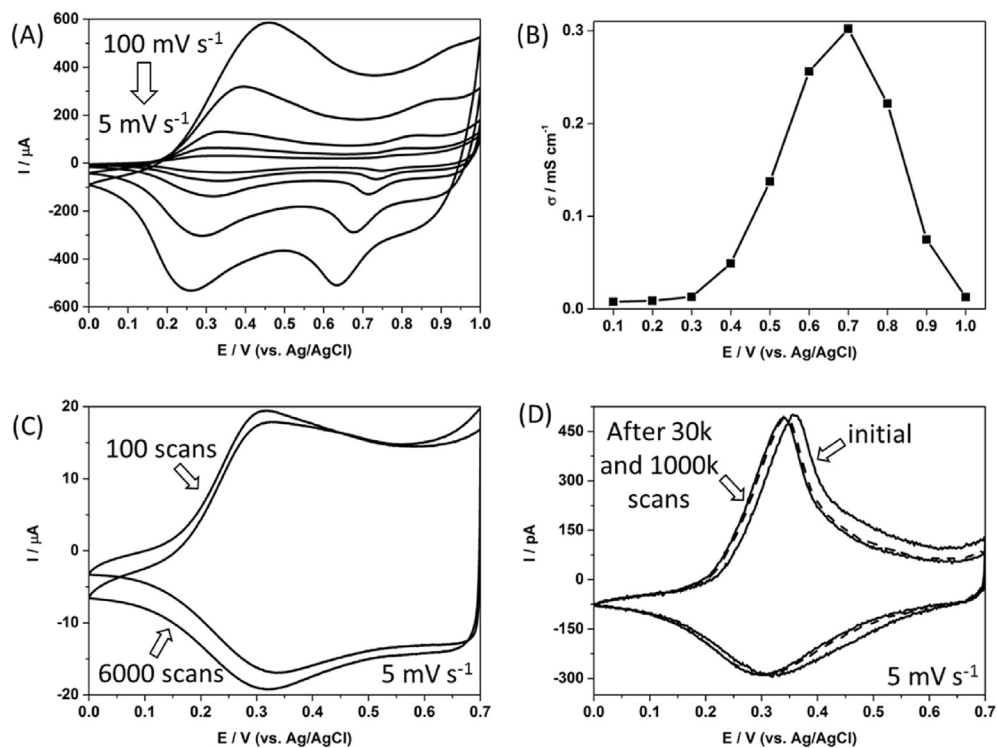
The electronic wire accessing the redox function of the monolignols should preferably be at least as longlived as the monolignol.

\* Corresponding author.

E-mail address: [ois@ifm.liu.se](mailto:ois@ifm.liu.se) (O. Inganäs).



**Fig. 1.** The hypothetical structure of PAAQ oligomers doped with sinapic acid (shown here as an example), and chemical structures of the dopant after oxidation (A). UV–vis spectrum of PAAQ film (B), together with SEM micrograph of film surface (insert). Resonance Raman spectrum of PAAQ material recorded with an excitation wavelength of 659 nm (C). Representative mass spectrum (MALDI-TOF) of PAAQ oligomeric films (D). Note: the molecular weight of the monomer is 223.23 g mol<sup>-1</sup>.



**Fig. 2.** Cyclic voltammograms of PAAQ films recorded in 0.1 M HClO<sub>4</sub> (aq.) shown as a variation of scan rate (A). The change in conductivity of PAAQ films in 0.1 M HClO<sub>4</sub> (aq.) vs. applied potential (B). Electrochemical stability of PAAQ films in 0.1 M HClO<sub>4</sub> (aq.) examined at macro- (C) and microelectrodes (D) recorded with the scanning speeds of 100 mV s<sup>-1</sup> and 10 V s<sup>-1</sup>, respectively.

This is not the case for polypyrrole, which has been used in previous studies of hybrids between electronic polymers and lignin. We have shown that degradation of the polypyrrole chain occurs at the

redox potential of the quinone deriving from lignin [12]. Better candidates are the conjugated polymers based on amino-anthraquinone (AAQ). Films made of AAQ macromolecules are

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