

FIRST Center Research Perspective:

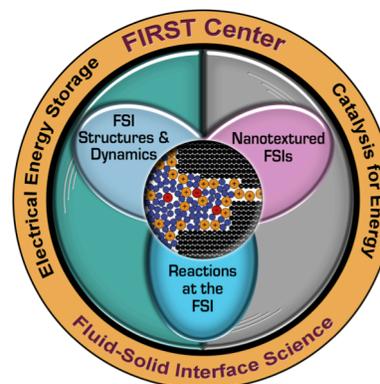
PCET Reactions and Sorption/Dynamics of Quinones on Carbon Surfaces with Pseudocapacitive Energy Storage Implications

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Research Summary: Proton-coupled electron transfer (PCET) is a fundamental process that underlies the kinetics of many reactions of energy relevance, including electrochemical water oxidation, CO₂ reduction and O₂ reduction reaction. These reactions occur at a fluid-solid interface and our challenge is to understand how the solvent/electrolyte distribution and properties and the surface and pore structures mitigate reaction processes. To probe PCET processes, we have explored model 2H⁺-2e⁻ redox reactions in adsorbed quinones. Our approach is to probe the adsorption, dynamics and redox of the molecules and proton donors at the fluid-solid interface. We have combined a variety of techniques to probe adsorption bonding and dynamics as well as electrochemical methods to probe the reactions.

Technical Details: Onion-like carbon (OLC) was used as substrate for adsorption of 9,10-phenanthrene quinone (PQ) for investigation of model system of proton-coupled electrochemical (PCET) reactions. The kinetics and pathways of redox reaction for the quinone/hydroquinone were investigated by cyclic voltammetry and in situ Raman spectroscopy in buffered and unbuffered aqueous electrolytes with different pH. The reaction kinetics and pathways are strongly dependent on the electrolyte pH and the presence of a buffer. The CV curves indicated that as the pH increases, the effects of confinement in the electrolyte-filled pores results in decreased availability of protons to diffuse to the vicinity of the sorbed PQ molecule, inhibiting the rate of reduction of PQ to PQH₂. Water, however, serves as an acceptor for the protons given off in the oxidation reaction, permitting rapid oxidation. At higher pH the buffer may act as a proton donor or acceptor in a concerted PCET reaction. Molecular changes during reduction

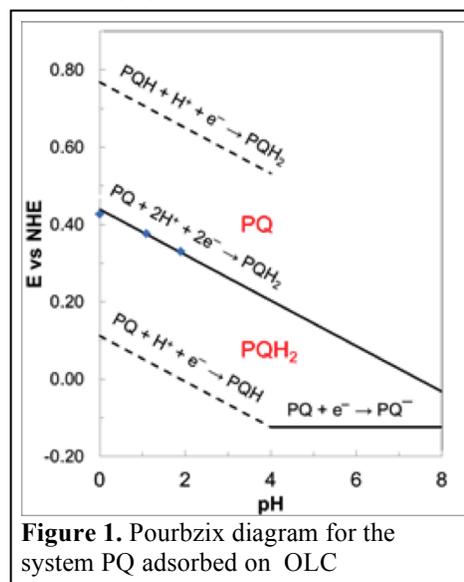
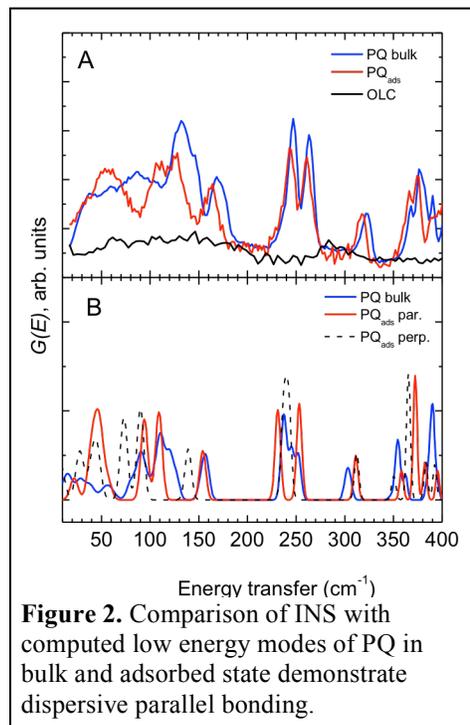


Figure 1. Pourbaix diagram for the system PQ adsorbed on OLC

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of PQ were followed by in situ electrochemical Raman spectroscopy (Raman-EC) which showed that at all pH the molecule is completely reduced during CV. Considering the reaction thermodynamics a Pourbaix diagram (**Fig. 1**) and a square scheme were constructed. These results demonstrate that the redox process to semiquinone occurs by a concerted electron-proton transfer reaction and that the semiquinone rapidly dis-proportionates to form the hydroquinone.

Further characterization of the PQ adsorption was performed using inelastic neutron scattering (INS) and Raman, and these results were linked to density functional theory (DFT) to probe the orientation and bonding of adsorbed PQ on OLC. Electrochemical measurements demonstrated relatively strong bonding of PQ to the OLC as indicated by persistent and reversible features in the cyclic voltammetry. Spectra of bulk solid and adsorbed PQ were obtained by Inelastic Neutron Scattering (INS) and Raman spectroscopy, and the bands were compared with vibrational energies calculated from DFT. At energy losses (frequencies) above 400 cm^{-1} , no band shifts in INS or Raman spectra were observed between bulk solid and adsorbed PQ. However, adsorption of PQ resulted in shifts in the lowest frequency modes ($< 400\text{ cm}^{-1}$), compared to crystalline bulk PQ, which could only be identified by INS (**Fig. 2A**). DFT calculations also provided adsorption energies and from comparison of computed and experimental spectra it is determined that the molecule adsorbs parallel to the onion-like carbon surface through π - π stacking interaction. (**Fig. 2B**)



We used quasielastic neutron scattering (QENS) to study the dynamics of PQ on the OLC, as a function of surface coverage and temperature. Two diffusion processes were observed; a faster process and nearly an order of magnitude slower process. On the high-coverage surface, the slow diffusion process is of long-range translational character, whereas the fast diffusion process is spatially localized on the length scale of $\sim 4.7\text{ \AA}$. On the low-coverage surface, both diffusion processes are spatially localized; on the same length scale of $\sim 4.7\text{ \AA}$ for the fast diffusion and a somewhat larger length scale for the slow diffusion. Arrhenius temperature dependence is observed except for the long-range diffusion on the high coverage surface. Unexpectedly, the dynamics of PQ molecules on OLC as a function of temperature and surface coverage bears qualitative resemblance to the dynamics of water molecules on oxide surfaces, including practically temperature-independent residence times for the low-coverage surface. The dynamic features that we observed may be universal across different classes of surface adsorbates.

We examined PQ adsorption on pristine graphene epitaxially grown on SiC (EG) by high-resolution X-ray interface scattering shown in **Fig. 3**. PQ deposited on pristine graphene is vulnerable in aqueous solutions (at least under electrochemical cycling) and does not exhibit stable adsorption state. Introduction of defects with reactive oxygen plasma was effective to promote adsorption of PQ on graphene basal plane, that showed the expected PCET reaction

behavior. XRR indicates adsorbed PQ lies parallel to the basal plane, as measured in-situ with X-ray reflectivity, and resembles the graphene layer stacking. The resultant PQ adsorption structure is intact as a function of electrochemical potential in aqueous solutions. These results provide a base-line for understanding relevant interactions between aromatic functional groups with graphene, leading to fundamentally new insights and providing unique tests of atomistic fluid-solid interface models for catalytic energy systems.

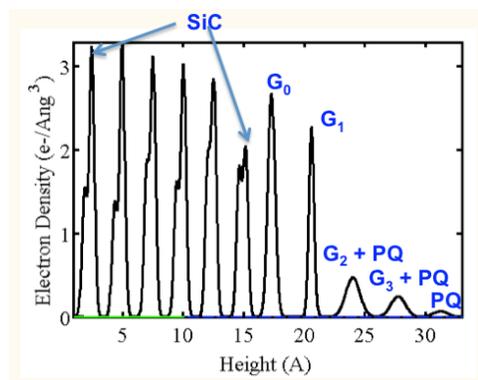


Figure 3 X-ray reflectivity data of an EG sample after oxygen plasma treatment PQ adsorption

Redox reactions of quinones on OLC has implications in energy storage. OLC can be used to obtain electrodes for supercapacitors with extremely high power handling. Quinone decoration of the exohedral surface of carbon onions increases the energy density by maximum 900%, from 0.5 Wh/kg to 4.5 Wh/kg. Charge storage and recovery associated with the electrical double layer and proton-coupled electron transfer in quinone-modified OLC electrodes contribute to the capacitive storage. The capacitance of 264 F/g is very high compared to the capacitance of unmodified OLC electrodes (≈ 30 F/g) or activated carbon onions and is stable for thousands of charge and discharge cycles. Studies were made for three different quinones. The smallest decrease of capacitance with increased scan rate was identified for the quinones with the highest binding energy to the OLC surface (i.e., 4,5-pyrenedione), the highest capacitance was found for the sample with the highest loading with quinone molecules. We conclude that quinone modification presents a facile way to significantly improve the energy density without sacrificing the cycling stability for electrical energy storage devices.

Significant Impacts on Science and Technology: Our results have provided a detailed description of a model $2\text{H}^+ - 2\text{e}^-$ reaction system. By detailed characterization of the system we are able to show that the reduction reaction occurs by a concerted electron and proton transfer and that this concerted process is responsible for lowering the reaction barrier, an electrocatalytic effect. The concepts provide a basis for understanding how such reactions may in many electrocatalytic applications. Additionally this work has shown how such molecular processes may be applicable to energy storage in pseudocapacitor type systems.

Publications and Manuscripts:

1. Anjos, D. M.; Kolesnikov, A.; Wu, Z.; Cai, Y.; Neurock, M.; Brown, G. M.; Overbury, S. H., Spectroscopy and bonding of phenanthrenequinone adsorbed on onion-like carbon: Inelastic neutron scattering and DFT investigations, *Carbon* **2013**, 52, 150-157.
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3. Anjos, D. M.; Wu, Z.; Brown, G. M.; Overbury, S. H., Buffer effect on the reaction pathway of 9,10-phenanthrenequinone adsorbed on nanostructured surface, *Journal Phys. Chem. B* **2013**, submitted.
4. Chathoth, S. M.; Anjos, D. M.; Mamontov, E.; Brown, G. M.; Overbury, S. H., Dynamics of Phenanthrenequinone on Carbon Nano-Onion Surfaces Probed by Quasielastic Neutron Scattering, *Journal of Physical Chemistry B* **2012**, 116, 7291–7295.