

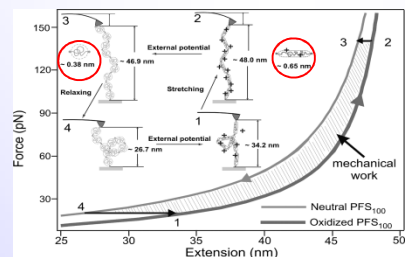


# POLY[FERROCENYLSILANE] BIOCOMPATIBLE ELECTROCHEMICALLY RESPONSIVE ACTUATORS

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## REDOX-DRIVEN MACROMOLECULAR MOTORS

In nature several classes of molecular motors fulfill different functions in the living cell [1]: proton pumps in membranes, motor proteins like myosin, DNA and RNA polymerases and flagellar motors in bacteria. Single molecule studies of various synthetic molecular motors may provide access to a more fundamental understanding of molecular scale processes. Future nanodevices such as levers, valves and pumps will require molecular motors to generate mechanical work as a consequence of appropriate external stimuli. Electrochemically switchable single polymer chains are possible candidates for these motors [2].



The Twente group has been developing **redox-driven macromolecular motors** by investigating various **stimuli-responsive poly[ferrocenylsilanes] (PFSs)**. PFS can reversibly be oxidized and reduced by external potentials which lead to changes in their mechanical properties and can be used to drive cyclic molecular motors. Studies of their closed mechano-electrochemical cycles were done using electrochemical AFM-based single-molecule force spectroscopy (SMFS).

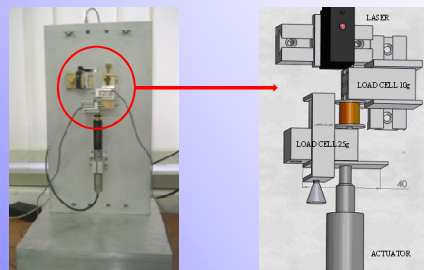
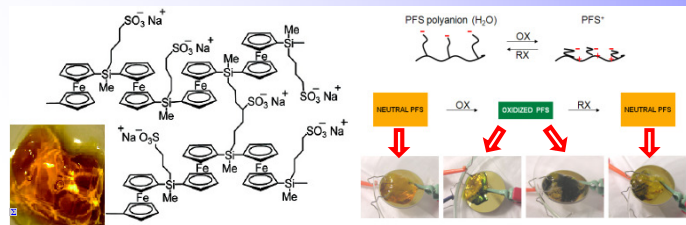
Oxidised chains lengthened compared to neutral ones, which is attributed to the electrostatic repulsion between the oxidized ferrocene centers along the chain. A **force of about 140 pN** on the AFM cantilever was detected upon redox stimulation, while a single pre-stretched PFS chain was fixed in position z. Single-chain efficiency was found to increase with increasing stretching ratio. Experimentally, a maximum **efficiency of 26%** was observed [3].

## REDOX-RESPONSIVE MACROSCOPIC PFS POLYANIONS

The current phase of research is to synthesise macroscopic PFS polymers to create **biocompatible electrochemically responsive actuators**, which expand and contract reversibly during redox. PFSs are ionic electroactive polymers (**EAPs**) which sense external stimuli and respond accordingly in real time. These smart materials are attracting increasing attention because of their potential use for building sensor-actuators which mimic muscles [4].

Recently redox-responsive PFS gels, which swell in organic solvents (THF, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>), have been created [5]. Since our aim was to obtain a biocompatible material, an organometallic **hydrogel** composed of redox-responsive PFS polyanion was synthesized, using covalent crosslinking [6a-b]. In this material the water is used as a solvent and electrolyte. Because of the side-group charges, our hydrophilic solid swells in water with a **swelling ratio of 120**. During oxidation, positive charges are formed on the main chain, causing the polyanion network to collapse, due to internal charge compensation. During reduction, the negative charges cause the polyanion network to expand.

## PFS POLYANIONIC HYDROGEL CHARACTERIZATION



Technologies to study viscoelastic materials adequately are difficult to find, therefore new measurement techniques and devices have been developed and prototyped by the Catania group. The **test machine** produced is able to mechanically and electrochemically characterise redox responsive hydrogels, with a **0.58% repeatability** using Young's modulus [6b-c-d].

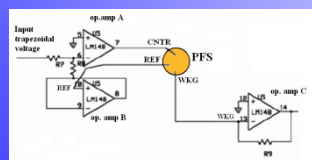
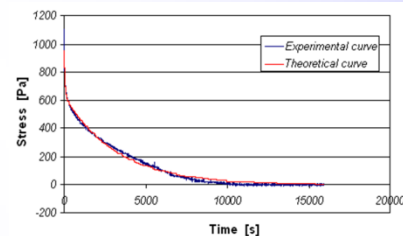
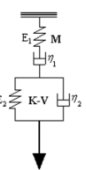
The mechanical characterization of soft materials is studied by **relaxation tests**. Our machine works in **Control Displacement-mode**, applying a static compression displacement to the sample and monitoring the stress. The **elastic modulus** was found between **1.5 ÷ 3.2 kPa**. An **experimental protocol** was produced to standardize the results for different tests.

The best theoretical **viscoelastic model** was the **Maxwell and Kelvin-Voigt in series**, which is described by the following four-parameter equation:

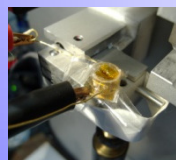
$$\sigma(t) = \frac{\epsilon_0}{p_1 - p_2} \left[ (E_1 p_1 + c) e^{p_1(t-t_0)} - (E_1 p_2 + c) e^{p_2(t-t_0)} \right]$$

The graph shows the comparison between the **experimental relaxation curves** and the **theoretical one**. The **standard deviation** between the two curves is **15.3 Pa**.

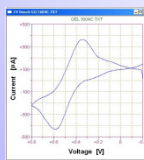
MAXWELL & KELVIN-VOIGT  
IN SERIES  
(Four parameters)



Potentiostat schematic circuit



Electrochemical experimental setup



Cyclic

The electrochemical characterization of EAPs is studied by **cyclic voltammetry (CV)**. Our hydrogel needs more time at oxidation peak, to obtain complete oxidation. So, a LabVIEW software to generate trapezoidal (not triangular) waves was created. A potentiostat, able to impose the potential wave across the working electrode relative to the reference electrode and to measure the resulting current through the material at the working electrode relative to the counter electrode, was built [7].

Upon reduction the polyanionic hydrogel expands whose generated thrust is proportional to sample size and therefore to integrated charge transfer. To create unidirectional thrust, the hydrogel was put inside a cylinder. For samples of 100 mm<sup>3</sup> the **thrust** measured was **50 Pa**.

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