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# Pico-electrochemistry in humidity-equilibrated electrolyte films on nano-cotton: Three- and four-point probe voltammetry and impedance

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ABSTRACT

Cotton-extracted cellulose nanocrystals are spin-coated from aqueous suspension (0.6 wt%) onto glass slides to give ca. 40 nm thick films. Impregnation with LiCl and redox active $Fe(CN)_6^{3-/4-}$ into this film gives extremely thin redox active layers (typically 170 nm at 60% relative humidity), which were investigated with a 4-point or 3-point probe electrochemical system based on 250 μm diameter platinum wire probes. Both voltammetry and impedance measurements were performed and effects from humidity, concentrations, and time domain on measurements are reported. Only a pico-litre volume under the working electrode was "active" to give a novel electroanalytical "spot test".



## 1. Introduction

Small-scale voltammetric analysis is desirable in particular for (i) analysis of expensive (e.g. bio-chemical) redox systems [1], (ii) multi-electrode [2] or high throughput multi-well analysis where thousands of samples need to be screened [3], and (iii) fast response films for example for gas sensing applications [4] where diffusion times need to be minimised. Conventional voltammetric cells operate with typically 10–100 $cm^3$ volume of solvents and in recent work on microfluidic devices this has been reduced to ca. $10^{-9}$ $cm^3$ [5]. Here, we aim to reduce this volume by yet another couple of orders of magnitude and propose a method where $10^{-12}$ $cm^{-3}$ sample volumes could be analysed routinely.

Analysis on cellulose substrates has a long history [6] with many types of pH and spot tests [7,8] as well as chromatography being performed. Paper and cellulose remain popular substrates for new types of electroanalytical methods based on micro-fluidic processes/systems on disposable sensors [9,10]. Nano-cellulose materials have opened up further opportunities in electroanalysis [11] with pure cellulose [12] or composite films [13,14] being readily re-constituted or regenerated, for example on ITO electrode surfaces [15]. Surface-modified nanocrystalline cellulose whiskers have been re-constituted into redox active films with electron transfer occurring between the ferrocene grafts along the nanocrystal surface [16].

Here, a thin film of cotton-extracted nanocrystalline cellulose (ca. 40 nm thickness) is formed via a spin-coating protocol. The glass slide with cellulose nanocrystals and impregnated with a very small volume of electrolyte is shown in Fig. 1A. Although almost invisible, the four-point probe measurements clearly reveal the presence of the nanoparticle film and the humidified electrolyte film with redox active components. In order to study the behaviour of the system both 3-point probe (Fig. 1B) and 4-point probe (Fig. 1C) experiments were performed for the model case of the one-electron $Fe(CN)_6^{3-/4-}$ redox system.

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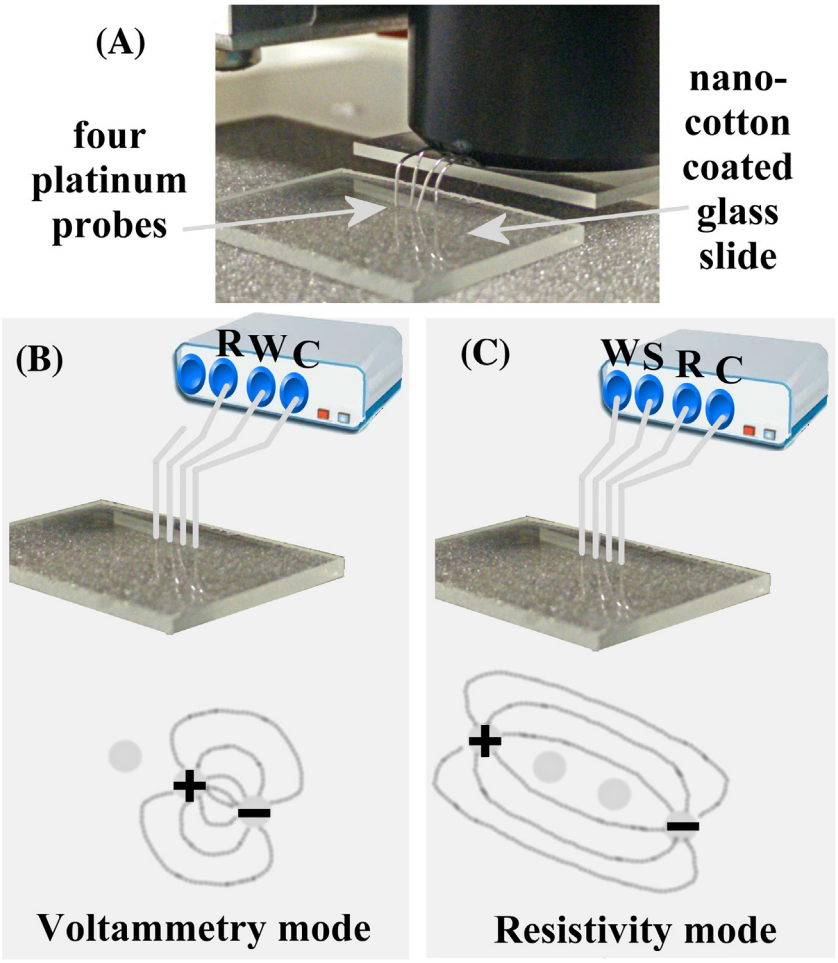


**Fig. 1.** (A) Photograph of the 4-point probe with 250 μm diameter platinum wires with approximately 1 mm inter-electrode gap positioned on a cotton-extracted nanocrystalline cellulose modified glass slide. (B) Schematic drawing of the 3-point probe configuration for voltammetry. (C) Schematic drawing of the 4-point probe configuration for resistance measurements.

## 2. Experimental

### 2.1. Chemical reagents

LiCl, $K_4Fe(CN)_6$, and $K_3Fe(CN)_6$ were obtained from Sigma-Aldrich or Fisons and used without further purification. Aqueous solutions were prepared using ultrapure water at 20 °C (resistivity ≥ 18.2 MΩ cm).

### 2.2. Extraction of cellulose nanocrystals from cotton

Nanocrystalline cellulose particles were extracted from pure cotton wool via acid hydrolysis using a 64 wt% aqueous sulfuric acid solution (8.75 ml $H_2SO_4$ solution per g of cotton) for 40 min at 45 °C under constant stirring. The obtained suspension was centrifuged three times with intermittent washes after quenching the reaction with an equal amount of cold deionized water. The suspension was then dialyzed against tap water to remove residual free acid. A stable dispersion was obtained by sonication (Branson sonifier 250, 10% amplitude in pulse mode, $T < 25$ °C) and filtration over a No. 2 fritted filter to remove aggregates. Ion exchange resin Amberlite MB 6113 was then added to the dispersion under agitation for 1 h to protonate the nanocrystal surface and remove non-$H^+$ ions. The ion exchange resin was removed by filtration followed by another sonication step to individualise the cellulose nanocrystals. The concentration of the final dispersion was determined to be 0.6 wt% by gravimetric analysis.

### 2.3. Instrumentation and procedures

Electrochemical measurements were performed at 20 ± 2 °C using an Autolab PGSTAT12 bipotentiostat (Metrohm, UK). A three- or four-electrode configuration was employed with 250 μm diameter platinum wire electrodes with the ends flame-cleaned before use. A Jandel 4-point probe stage was employed initially with standard WC probes (which gave unreliable voltammetry due to more complex electron transfer) and then with platinum wire probes. Relative humidity was measured with a TFA Dostmann/Wertheim sensor. A WS-650Mz-23NPP (Laurell Technologies) spin coater was used to spin the cellulose nanocrystals from a 0.6 wt% aqueous suspension onto glass slides (prepared from microscopy slides). Scanning electron microscopy (SEM) images were obtained after 5 nm chromium coating with a JSM-6480LV (JEOL, Japan) and analysed using imageJ 1.48 v software. Atomic Force Microscopy (AFM) images were obtained using a Digital Instruments Nanoscope IIIa Multimode Scanning Probe Microscope in tapping mode (Veeco TESP probes).

### 2.4. Film formation

A solution of 0.6 wt% of nano-cotton in water was spin-coated onto a glass slide (cleaned by heat treatment for 30 min at 450 °C)