

Coding for Hydrogel Organization through Signal Guided Self-assembly

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Moving Front Model

Assumptions:

1. The rate of chitosan deprotonation is assumed to be equal to the rate of electron transfer at the cathode (i.e., the current i). This assumption essentially states that base generated at the cathode is exclusively used for chitosan deprotonation. In essence, this moving front model also assumes that deprotonation is irreversible and that none of the base generated at the cathode diffuses into the bulk to change the bulk pH. Obviously, this assumption is an approximation and is supported by observations of a steep pH gradient across the gel front.¹ This assumption is valuable because it allows the readily measured cumulative charge transfer (Q) to be related to the extent of deprotonation (N_{Deprot} ; μmole) using the Faraday constant (F).

$$N_{Deprot} = \frac{Q}{F} = \frac{1}{F} \int i dt \quad (1)$$

2. Chitosan chains within the gel are assumed to be completely deprotonated while those in the bulk are assumed to be completely protonated. This assumption provides the stoichiometric relation between deprotonation (i.e., equation (1)) and gelation. This assumption neglects the number of chitosan's glucosamine residues that are deprotonated in the bulk solution. The number of deprotonated glucosamine residues at pH 5 is expected to be small. We also neglect the degree of deacetylation by assuming chitosan is fully deacetylated. We considered the degree of deacetylation to be a second-order concern for the model.
3. The chitosan concentration (C) is assumed to be constant everywhere although the protonation state of a chitosan molecule depends on which side of the front it is located. This latter assumption ignores the migration of chitosan chains to the electrode. The amount of chitosan in this growing gel (N_{Gel} ; μmole) is quantified as the number of deprotonated glucosamine residues ($M=161 \text{ g/mole}$).

Experimental Values:

The volume of the deposited gel (V_{Gel}) can be determined using geometric considerations of a wire of radius ($r=0.2$ mm) immersed in the deposition solution to a depth ($l=25$ mm), and a chitosan film deposited to a radius R (experimentally measured).

$$N_{Gel} = \frac{CV_{Gel}}{M} = \frac{C}{M} \pi l (R^2 - r^2) \quad (2)$$

When a chitosan concentration is 1 % (10 g/L) was used in experiments and this is converted to a molar basis of glucosamine residues per mm^3 by:

$$\frac{C}{M} = \left(\frac{10\text{g}}{\text{L}} \right) \left(\frac{1\text{mol}}{161\text{g}} \right) \left(\frac{10^{-3}\text{L}}{\text{cm}^3} \right) \left(\frac{10^{-3}\text{cm}^3}{\text{mm}^3} \right) = 6.21 \times 10^{-8} \text{ mole/mm}^3$$

Volume of the cylindrical shell of deposited chitosan: $V_{Gel} = \pi l (R^2 - r^2)$

Supplementary Images for Figure 2

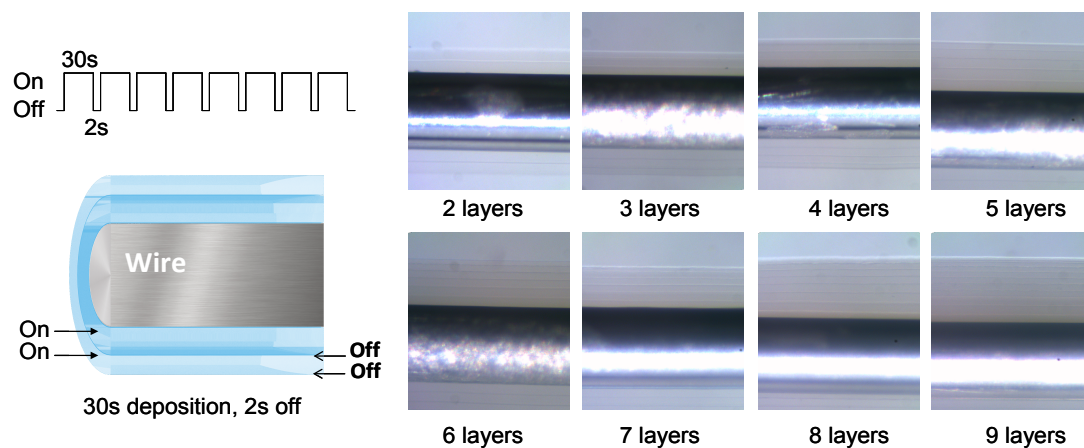


Figure S1. Optical images of sequential layer construction by applying predetermined number of “on-steps” (30 s) and “off-steps” (2 s).

1. Cheng, Y.; Luo, X. L.; Betz, J.; Buckhout-White, S.; Bekdash, O.; Payne, G. F.; Bentley, W. E.; Rubloff, G. W. *Soft Matter* **2010**, 6, (14), 3177-3183.