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### Can the wet - State conductivity of hydrogels be improved by incorporation of spherical conducting nanoparticles?

Katharina Schirmer

*University of Wollongong, ksus852@uowmail.edu.au*

Cody Wright

*University of Wollongong, cjw684@uowmail.edu.au*

Holly Warren

*University of Wollongong, hwarren@uow.edu.au*

Brianna C. Thompson

*University of Wollongong, brianna@uow.edu.au*

Anita F. Quigley

*University of Wollongong, anitaq@uow.edu.au*

*See next page for additional authors*

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## Can the wet - State conductivity of hydrogels be improved by incorporation of spherical conducting nanoparticles?

### Abstract

In nerve and muscle regeneration applications, the incorporation of conducting elements into biocompatible materials has gained interest over the last few years, as it has been shown that electrical stimulation of some regenerating cells has a positive effect on their development. A variety of different materials, ranging from graphene to conducting polymers, have been incorporated into hydrogels and increased conductivities have been reported. However, the majority of conductivity measurements are performed in a dry state, even though material blends are designed for applications in a wet state, in vivo environment. The focus of this work is to use polypyrrole nanoparticles to increase the wet-state conductivity of alginate to produce a conducting, easily processable, cell-supporting composite material. Characterization and purification of the conducting polymer nanoparticle dispersions, as well as electrochemical measurements, have been performed to assess conductivity of the nanoparticles and hydrogel composites in the wet state, in order to determine whether filling an ionically conducting hydrogel with electrically conductive nanoparticles will enhance the conductivity. It was determined that the introduction of spherical nanoparticles into alginate gel does not increase, but rather slightly reduces conductivity of the hydrogel in the wet state.

### Keywords

can, spherical, wet, conducting, nanoparticles, state, conductivity, hydrogels, be, improved, incorporation

### Disciplines

Engineering | Physical Sciences and Mathematics

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### Authors

Katharina Schirmer, Cody Wright, Holly Warren, Brianna C. Thompson, Anita F. Quigley, Robert M. I Kapsa, and Gordon G. Wallace

# Can the Wet – State Conductivity of Hydrogels be Improved by Incorporation of Spherical Conducting Nanoparticles?

Katharina Schirmer<sup>1</sup>, Cody Wright<sup>1</sup>, Holly Warren<sup>2</sup>, Brianna Thompson<sup>1,3</sup>, Anita Quigley<sup>1,4</sup>, Robert Kapsa<sup>1,4</sup> and Gordon Wallace<sup>1</sup>

<sup>1</sup> ARC Centre for Electromaterials Science and Intelligent Polymer Research Institute, AIIM Facility, Innovation Campus, University of Wollongong, Australia

<sup>2</sup> ARC Centre of Electromaterials Science and Soft Materials Group, AIIM Facility, Innovation Campus, University of Wollongong, Australia

<sup>3</sup> School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore

<sup>4</sup> Department of Clinical Neurosciences, St Vincent's Hospital, Melbourne and Department of Medicine, The University of Melbourne, Australia

## ABSTRACT

In nerve and muscle regeneration applications, the incorporation of conducting elements into biocompatible materials has gained interest over the last few years, as it has been shown that electrical stimulation of some regenerating cells has a positive effect on their development. A variety of different materials, ranging from graphene to conducting polymers, have been incorporated into hydrogels and increased conductivities have been reported. However, the majority of conductivity measurements are performed in a dry state, even though material blends are designed for applications in a wet state, *in vivo* environment. The focus of this work is to use polypyrrole nanoparticles to increase the wet-state conductivity of alginate to produce a conducting, easily processable, cell-supporting composite material. Characterization and purification of the conducting polymer nanoparticle dispersions, as well as electrochemical measurements, have been performed to assess conductivity of the nanoparticles and hydrogel composites in the wet state, in order to determine whether filling an ionically conducting hydrogel with electrically conductive nanoparticles will enhance the conductivity. It was determined that the introduction of spherical nanoparticles into alginate gel does not increase, but rather slightly reduces conductivity of the hydrogel in the wet state.

## INTRODUCTION

In the last two decades, there has been recognition of the importance of electric fields in guiding and manipulating tissue patterning, development and function across many tissue types<sup>1-3</sup>, the implication being that the ability of biomaterials to conduct electricity has become more important<sup>4</sup>. One class of materials, which has been widely used for many applications as a biomaterial, is hydrogels<sup>5-7</sup>. Hydrogels can be tailored in their mechanical properties to suit specific tissue engineering applications as well as deliver growth factors and cells to the site of implantation<sup>8,9</sup>. Some hydrogels, such as sodium alginate, are ionically conducting, as the ions in the gel act as charge carriers; however, they are not considered to be sufficiently conductive for applications such as cell stimulation.

Electrically conducting particles with high aspect ratios made from different materials have been successfully used as fillers to reduce the resistivity and improve mechanical properties

of gels<sup>10, 11</sup>. Spherical particles, however, are thought to show better biocompatibility<sup>12-15</sup>. The majority of conductivity measurements are performed in a dry state where the materials are dehydrated and compacted, potentially changing their percolation threshold and, therefore, capacity to conduct electricity, even though materials are proposed for applications in a wet *in vivo* environment.

In this work, spherical polypyrrole nanoparticles and silver nanoparticles are blended with alginate gel and the effects on conductivity are analyzed in the wet state to approximate physiological conditions, using an adapted electrochemical impedance spectroscopy setup.

## **THEORY AND EXPERIMENT**

### **Polypyrrole Nanoparticle (PPyNP) Synthesis**

To synthesize polypyrrole nanoparticles, 0.5 wt% polyvinyl alcohol (PVA, MW 31 – 50 kDa, Sigma-Aldrich) was added to MilliQ water at 80°C and stirred until fully dissolved. The solution was cooled to 4°C before 0.05 M of iron (III) p-toluenesulfonate hexahydrate (FepTS, Sigma-Aldrich) was added and stirred until fully dissolved. The polymerization was initiated with the addition of 0.01 M pyrrole monomer solution (Merck Millipore, distilled) and continued for at least 8 h at 4°C before the particle dispersion was dialysed against MilliQ water for at least 48 h (with water changes every 12 h) using cellulose dialysis tubing with an average molecular weight cut off (MWCO) of 12 – 14 kDa (Sigma-Aldrich). To remove excess PVA, the dispersions were concentrated and then washed in MilliQ water using centrifugal filter units with a MWCO of 100 kDa (Amicon Ultra, Merck Millipore). Washed dispersions were removed from the filters and freeze dried. Filtered particles synthesised in this manner have a spherical shape and an average size of  $63 \pm 3$  nm measured by scanning electron microscopy.

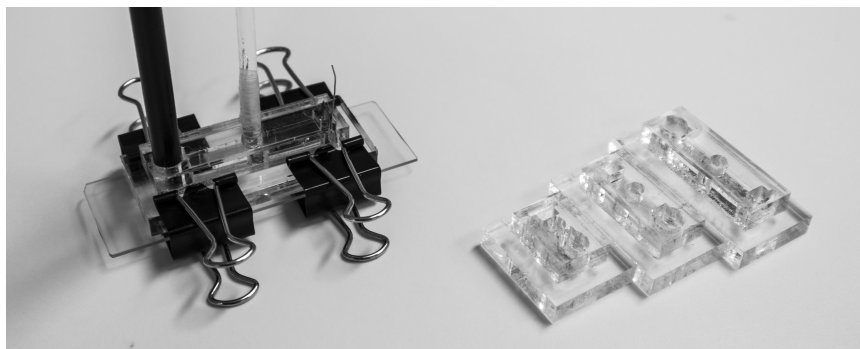
### **Silver Nanoparticle (AgNP) Synthesis**

Citrate-decorated silver nanoparticles were synthesized based on an adapted method from Lee and Meisel<sup>16</sup> with increased concentrations: 500 mL of a 2.1 mM solution of silver nitrate (Sigma) was brought to a boil, to which 20 mL of 1% sodium citrate was added and mixed at temperature until a colour change was observed. This reaction was repeated three times, before the overall volume of 1.5 L was reduced to 12 mL via freeze-drying to achieve a particle concentration of 2.5 wt% in water. Using dynamic light scattering analysis the average particle size was shown to be  $58 \pm 2$  nm.

### **Electrochemical Impedance Spectroscopy (EIS) on Gels**

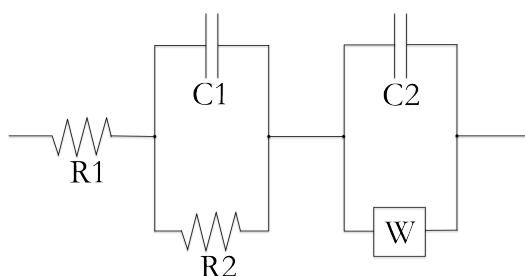
Freeze dried PPyNPs were mixed with 2%(w/v) sodium alginate gel (alginic acid sodium salt from brown algae, medium MW from Sigma Aldrich, dissolved in MilliQ water) at a concentration of 5%(w/v). Sodium alginate was added to the 2.5 wt% AgNP dispersion at a concentration of 2%(w/v). These solutions will be referred to as PPyAlg and AgAlg, respectively. Additionally to the solutions containing nanoparticles, pure sodium alginate gels at 2%(w/v) (2% Alg) and 4%(w/v) (4% Alg) in MilliQ water, as well as 2%(w/v) alginate containing the same concentration of sodium nitrate ( $\text{AlgNaNO}_3$ ) as the calculated excess in the

AgNP solution (0.71 M), were analysed using a custom-made EIS setup. Moulds to hold the gels were fabricated in 4 different lengths (1, 2, 3 and 4 cm) from Acrylic sheets, allowing the exact positioning of the working-, reference- and counter electrodes in the 3-electrode cell. In this study the electrodes used were glassy carbon as the working, platinum mesh as the counter and silver/silver chloride (Ag|AgCl) as the reference, shown in Figure 1.



**Figure 1:** Electrochemical cell setup consisting of different length moulds and a standard 3-electrode setup.

Using a CHI660D electrochemical workstation, EIS was performed from -0.5 V to 0.5 V (vs. Ag|AgCl) in 0.1 V steps starting from 0 V with increasing potential magnitude applied, each between 0.1 Hz to  $10^6$  Hz with an amplitude of 0.01 V. Before and after each set of EIS measurements cyclic voltammetry was performed to ensure no electrode plating had occurred. This was repeated over at least three different lengths, for all materials. The Nyquist plots of all gels, applied potentials and lengths were fitted to the model shown in Figure 2. The model consists of a resistor in series with two parallel circuits, the first being a resistor parallel with a standard RC-circuit, the second consisting of a capacitor and Warburg element. The overall resistance was calculated from the modeled R1 and R2 values, which were plotted over the different distances.



**Figure 2:** Electric circuit used to model Nyquist plots, with total resistance of the gel taken as the sum of R1 and R2.

## DISCUSSION

The onset and dip of the semi circle of the Nyquist plots in Figure 3 and 4 represent the relative resistance of the respective solutions. Shifting of the onset and dip of the semi circles towards the right (higher  $Z'$ ) indicates a higher resistive component of the impedance of the solution. The relative capacitance can be estimated from the highest point of the semicircle: higher semicircle apex values on the y-axis indicate higher capacitance of the solution. As Figure 3A shows no significant difference in relative resistance was found between the corresponding

positive and negative voltages applied for each gel. Representatively, Nyquist plots at 0.1 V, -0.1 V, 0.3 V, -0.3 V, 0.5 V and -0.5 V for 2% Alg gels are shown. As expected, a slight decrease in relative resistance and capacitance was observed with an increase in voltage magnitude applied. Figure 3B shows Nyquist plots of 2% Alg gel at 0.3 V over 1 cm (circle), 2 cm (triangle), and 3 cm (square) distance. As expected, the resistance and capacitance of the solution increases with distance.

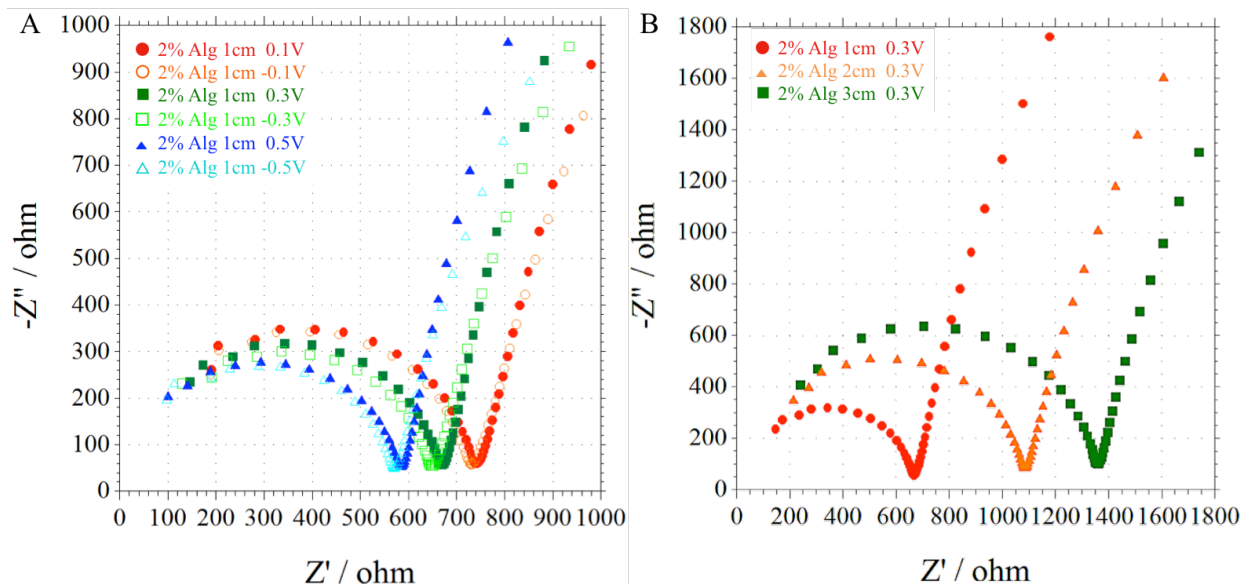


Figure 3: Nyquist plots of 2% alginate gel at different applied positive and negative potentials applied (A) and over different distances (B).

The combined resistance values, extracted from the fitting of the above model are summarized for all materials and distances in Table I. As can be seen from the Nyquist plots shown in Figure 4, the resistance and capacitance of pure alginate decreases with an increase in the concentration from 2% Alg (circle) to 4% Alg (star), due to the increase of ions per unit volume associated with the increased concentration of alginate salt. With addition of 5% PPyNPs to 2% alginate gel (PPyAlg, square) the resistance and capacitance of the gel increases. AgNPs blended with 2% alginate gel (AgAlg, triangle) results in a reduction of the resistance. This was determined to be due to the additional sodium and nitrate ions in the gel, which were added with the AgNPs as the change in resistance could be reproduced by the addition of the same concentration of  $\text{NaNO}_3$  to the alginate gel alone (Alg  $\text{NaNO}_3$ , diamond). Again, it can be observed that the addition of conducting nanoparticles, at the given concentrations, into an already ionically conducting hydrogels only hinders the ionic conductivity and does not improve the overall conductivity of the material.

Table I: Summary of resistance values for all materials and all distances

Resistance	1cm	2cm	3cm	4cm
<b>2% Alg</b>	$551 \pm 51 \, \Omega$	$919 \pm 69 \, \Omega$	$1267 \pm 91 \, \Omega$	-
<b>4% Alg</b>	$447 \pm 55 \, \Omega$	$740 \pm 97 \, \Omega$	$803 \pm 89 \, \Omega$	-
<b>PPy Alg</b>	$713 \pm 72 \, \Omega$	$1358 \pm 136 \, \Omega$	$1912 \pm 141 \, \Omega$	-
<b>Ag Alg</b>	$151 \pm 25 \, \Omega$	$219 \pm 30 \, \Omega$	-	$294 \pm 24 \, \Omega$
<b>Alg <math>\text{NaNO}_3</math></b>	$117 \pm 14 \, \Omega$	$159 \pm 17 \, \Omega$	$189 \pm 23 \, \Omega$	$234 \pm 22 \, \Omega$

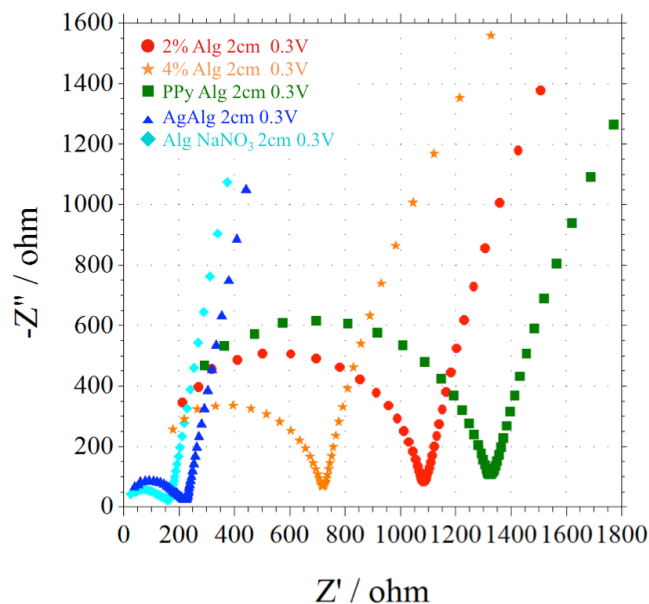


Figure 4: Nyquist plots of 2% alginate gel (circle) 4% alginate gel (star), 2% alginate gel containing 5% polypyrrole nanoparticles (square), 2% alginate gel containing 2% silver nanoparticles (triangle) and 2% alginate gel containing additional  $\text{NaNO}_3$  (diamond), all over a distance of 2 cm with 0.3 V vs. Ag|AgCl applied.

The EIS data was modelled and the overall resistance determined for each material over different distances, allowing resistivity of each material to be determined (see Figure 5B). The slope of the graphs in Figure 5A represent the resistivity in  $\text{ohms cm}^{-1}$ , with a steeper slope indicating a higher resistivity of the material. The conductivity of alginate gel increases proportionally to the concentration of the gel, and hence the amount of ions present.

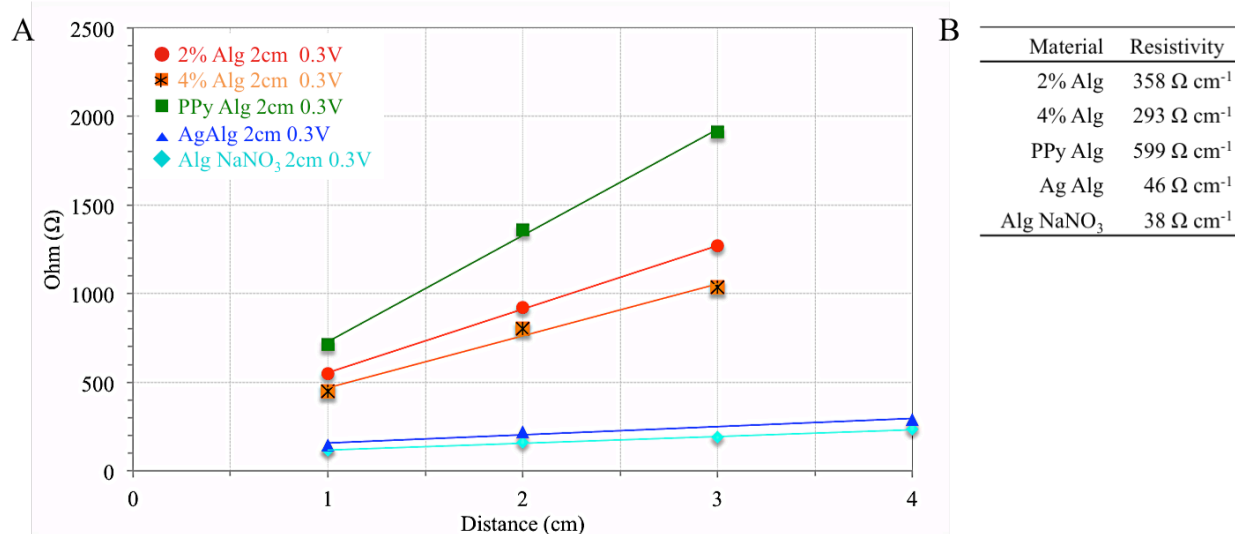


Figure 5: The resistance of different materials over different distances was extracted from EIS data fitted to the model shown in Figure 2. The resistance values for each material at different distances are shown (B). The slope of the plotted graphs represents the resistivity of the materials in  $\text{ohms cm}^{-1}$ .

## CONCLUSIONS

A reliable and detailed method has been developed and tested, allowing analysis of the conductivity of gels in wet-state, *in vivo* – like environment. Introduction of spherical PPyNPs at up to 5 wt% into alginate gel at 2% and 4% did not increase the electronic conductivity over the ionic conductivity of the gel itself. Instead the resistance is increased as the particles physically hinder ionic movement. This was proven by the addition of spherical, inherently highly-conducting AgNPs, which again increase the resistivity compared to an alginate containing an equivalent concentration of ions, showing that spherical, inherently conducting nanoparticles could not increase the conductivity in ionically conducting alginate gel.

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