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Energy Reports 7 (2021) 15–19
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5th Annual CDT Conference in Energy Storage & Its Applications, Professor Andrew Cruden, 2021, 01–12, held virtually

Cell design for the electrodeposition of polyacrylonitrile onto graphite composite electrodes for use in lithium-ion cells

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Received 17 February 2021; accepted 18 February 2021

Abstract

Polyacrylonitrile (PAN) is among the most common polymer materials in the world thanks to its versatility in a wide range of applications. Of importance to this work is its use in electrochemical cells. PAN has seen use as a separator material and as a binder material in lithium-ion cells. Expanding upon innovations made in recent decades for electrodepositing PAN onto conductive surfaces, this work details methods used to apply PAN as a thin coating to graphite composite electrodes; the resultant films may then be used for further electrochemical analysis in a lithium-ion cell. Graphite electrodes coated with electrodeposited PAN films were produced of a practical size for electrochemical testing in Swagelok cells; optical microscopy images of the resulting PAN coated graphite electrodes were also recorded to study the morphology of the coating.
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Peer-review under responsibility of the scientific committee of the 5th Annual CDT Conference in Energy Storage & Its Applications, Professor Andrew Cruden, 2021.

Keywords: Lithium battery; Cell design; Polyacrylonitrile

1. Introduction

In 1982, Lécayon et al. [1] published a pioneering report demonstrating the effective electrografting of polyacrylonitrile (PAN) onto metal surfaces. The report showed that metal surfaces can be coated with PAN films by using an electropolymerisation approach induced by the cathodic reduction of the polymer monomer (acrylonitrile, AN). It was proposed that the polymerisation initiated with the reductive adsorption of one monolayer of the monomer on the metal surface, which was assumed to involve one electron per adsorbed molecule. It was found that the PAN film coatings had very good adhesion to the metal electrode, which was ascribed to the formation of a chemical bond between the polymer and the metal surface, shown in Fig. 1 [2,3].

More recently, Lacey et al. [4] and El-Enany et al. [5] studied the electrodeposition of PAN onto glassy carbon and found that in the presence of oxygen the polymerisation started at less cathodic potentials. This was ascribed to the involvement of a superoxide species, formed as the product of the one electron reduction of oxygen, in

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https://doi.org/10.1016/j.egyr.2021.02.061
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Nomenclature

AN	Acrylonitrile
PAN	Polyacrylonitrile

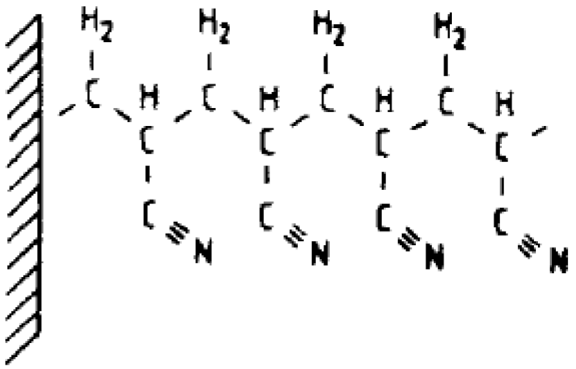

Fig. 1. Structure of the electrografted PAN on metal electrodes, formed via cathodically induced anionic polymerisation [2,3].

the electropolymerisation process. Using electrochemical quartz crystal micro balance experiments, combined with cyclic voltammetry measurements, they demonstrated the successful deposition of the polymer on the glassy carbon electrode. However, the mechanism of electropolymerisation in the presence of oxygen is not fully understood and it is not clear if the involvement of superoxide affects the final structure of the polymer coating. A critical factor required for good adhesion of the polymer on the metal electrode is the preservation of the chemical bond between the electrode and the polymer.

Earlier work by Baute et al. [6] and Mertens et al. [7] demonstrated that the potential employed for the cathodic polymerisation critically affects the final structure of the polymer coating. By performing electrochemical quartz crystal micro balance experiments, coupled with cyclic voltammetry measurements, they could identify that when the electrodeposition was made at mildly cathodic potentials, close to the onset of the electroreduction of the monomer, then a polymer coating firmly anchored to the electrode was obtained. However, when the electrodeposition was performed at more cathodic potentials, then the attachment of the polymer coating to the electrode was weak.

In this work, we have developed a new cell design that enables the systematic study of electrodeposition of PAN on different types of electrodes, in the presence and absence of oxygen. The cell is particularly useful to investigate the electrodeposition of PAN on battery composite electrodes, which can have different types of applications like the construction of 3D batteries [8] .

2. Experimental

2.1. Material preparation

Materials used to prepare PAN depositing electrolyte, all sourced from Sigma-Aldrich, were: ≥99% AN solvent with 35–45 ppm monomethyl ether hydroquinone inhibitor, 95% CaH_2 drying agent, ≥99% TBAP supporting electrolyte. PAN deposition largely replicated the work of Lacey et al. [4] and El-Enany et al. [5] using an AN solvent with 0.05 mol dm^{-3} TBAP supporting electrolyte. Solvents were distilled at 90–100 °C over CaH_2 under N_2 gas for at least 8 h to remove water. TBAP was dried beforehand under vacuum for 24 h. Electrolyte materials were prepared in a N_2 environment glovebox before being subsequently mixed in a N_2 flushed ampoule. After each deposition attempt, electrodes were left to dry in air for 24 h before being washed in ethanol for 10 min and left to dry for a further 24 h to remove the TBAP.

Depositions were performed on graphite composite electrodes. These graphite composite electrodes allowed anodes of 11 mm diameter sizes and greater to be made for testing in lithium-ion half-cell arrangements, allowing a more reliable measurement of cell performance in a practical cell arrangement. Preparation of the graphite composite electrodes was as follows:

1. Weigh a mixture of graphite active material (99% sourced from Hitachi Chemical), super C65 carbon black conductive additive (99% sourced from Timcal), and PVDF binder (average molecular weight ∼534000 by GPC powder sourced from Sigma Aldrich); the ratio should be 94:3:3 by weight, weights used 3.7 g : 0.12 g : 0.12 g.
2. Add 6.7 mL NMP (99.5% sourced from Sigma-Aldrich) to the mixture; NMP is a solvent in which PVDF is soluble and allows proper binding.
3. The mixture vial was then placed in a Thinky Planetary Mixer and mixed for a total of 15 min at 2000 rpm. This produces an electrode ink.
4. The ink was spread onto a polished copper foil surface, 0.05 mm thickness 99.9% purity (sourced from Advent). Spreading performed with a TQC Shean Dr blade set to an ink thickness of 0.25 mm, 200 mm s^{-1}. An ink area around 250 × 150 mm was obtained.
5. The ink was left to dry in a vacuum oven at 80 °C for 2–3 h.
6. Electrodes were cut to size and pressed at 10 tonnes for 1 min to improve particle density.

2.2. Electrodepositing cell

For the purposes of deposition, the graphite surfaces formed the working electrode in a three-electrode cell arrangement. A platinum gauze counter electrode and silver wire pseudo reference were used as the other two electrodes. Oxygen gas was introduced into the system via a gas sparger for 15 min to ensure full saturation of the electrolyte with oxygen. PAN electrodepositions were made in a custom Teflon cell (see Fig. 2). The Teflon cell has a 14 mm diameter channel between the graphite composite electrode and the counter electrode. The channel is sealed on the graphite side with a Teflon O-ring, which is stable in AN solvent, stopping contact between the electrolyte and the copper foil on the reverse side of the electrode. The 14 mm channel allows PAN deposited films of consistent size to be made on a scale that is practical for further electrochemical testing in Swagelok cells.

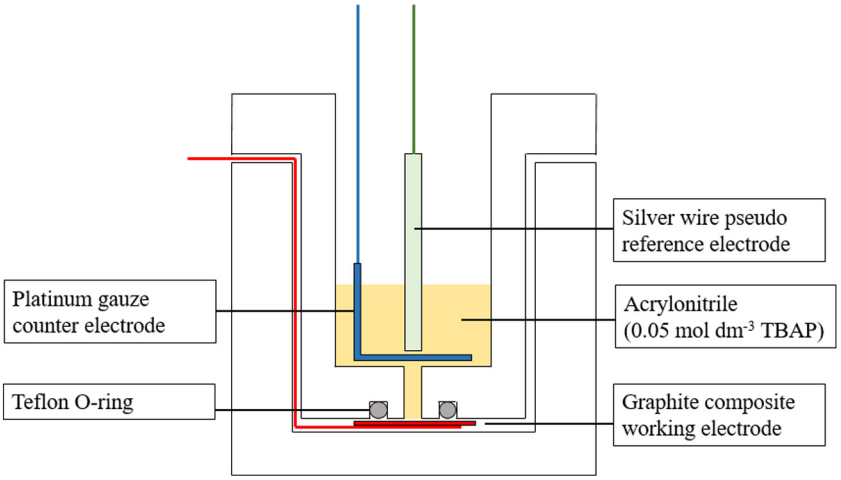

Fig. 2. Schematic of the Teflon cell used in PAN electrodepositions. Figure not to scale.

Cyclic voltammetry was employed to scan the potential and induce the electropolymerisation. The potential window used was −0.0 V to −3.5 V vs. the Ag pseudo-reference electrode. The scan rate used was 50 mV s^{-1}, and 5 cycles were recorded. Film thicknesses were then measured using an 'External Digital Micrometre, 0–25 mm/0–1 inches' from RS Components. Microscopy images of the resulting films were taken using optical microscopy at 10X magnification.

3. Results and discussion

Fig. 3 shows the first and second cycle voltammogram for the electrodeposition of PAN onto a composite graphite electrode using the Teflon cell shown in Fig. 2. The shape of the voltammogram and peak potential value is

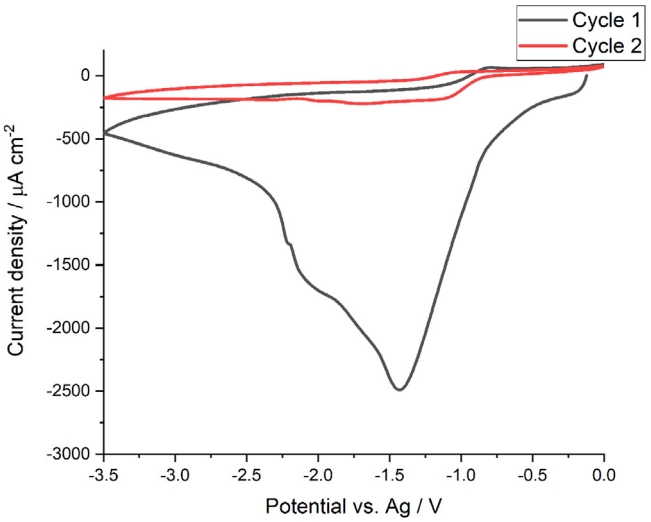

Fig. 3. First and second cycle voltammograms for PAN deposition onto a 14 mm diameter graphite composite electrode in a Teflon cell using AN(0.05 mol dm^{-3} TBAP) electrolyte saturated with oxygen. A scan rate of 50 mV s^{-1} from −0.0 V to −3.5 V vs. a silver pseudo reference electrode was used.

reasonably in agreement with the results reported by Lacey et al. [4]. The peak at −1.45 V is consistent with oxygen reduction to superoxide anion formation, which was proposed to initiate the polymerisation. The surface of the electrode is almost entirely passivated after the first cycle as current is reduced to near zero in later cycles. However, despite passivation of the electrode surface, leading to little current being passed, the film thickness will continue to increase if the cycle number is increased. After the first cycle a film thickness of 32 μm ± 1 μm was recorded and 80 μm ± 1 μm was recorded after the fifth. This would seem to indicate that only the initial reduction of oxygen and initiation of PAN are electrochemically driven, whilst further chain growth and propagation is chemically driven and limited by diffusion of monomers to the polymerisation sites.

Fig. 4 shows the optical microscopy images of a clean graphite composite and a graphite composite coated with PAN after five cyclic voltammetry cycles. The coating is immediately obvious, with the particles of graphite becoming covered by a film of PAN. However, cracks can be observed in the film. These cracks appeared after

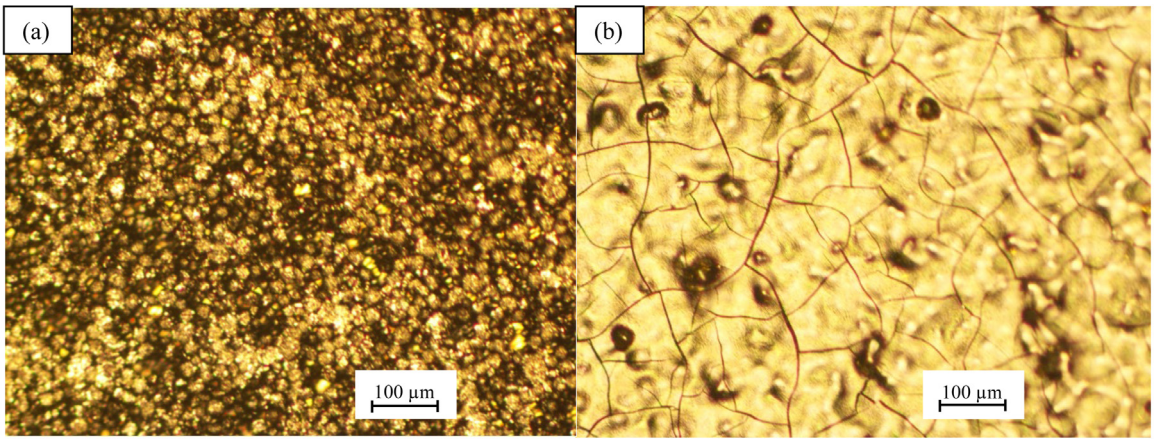

Fig. 4. (a) Optical microscopy image at 10X magnification of clean graphite composite electrode, (b) Optical microscopy image at 10X magnification of a graphite composite electrode coated with PAN after five cyclic voltammetry electrodeposition cycles.

electrodeposition when the AN(0.05 mol dm^{-3} TBAP) electrolyte evaporated. This would indicate that the cracks are caused by stresses due to volume loss of the AN solvent.

4. Conclusion

PAN was successfully deposited onto graphite composite electrodes using methods previously investigated for electrodeposition of PAN onto glassy carbon and other metal surfaces. The Teflon cell design allowed for practical sizes of coated electrodes, large enough to be practical for electrochemical testing in Swagelok cells. The deposition of PAN reliably produced films of similar thickness if cycled for a similar number of voltammetry cycles. However, the thickness does not appear to be controlled by the amount of current passed indicating that the propagation of chains is chemically driven and not electrochemically. Optical microscope images showed that the films showed signs of cracking. Further work is required to determine if this is a result of the solvent drying.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Funding provided by the Centre for Doctoral Training in Energy Storage and its Applications and the Engineering and Physical Sciences Research Council (EPSRC).

Acknowledgement

I would like to express my gratitude to the “EPSRC, United Kingdom, Centre for Doctoral Training in Energy Storage and its Applications” for the funding and opportunities presented during my research under the CDT grant code EP/L016818/1.

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