



# Processing of aqueous polymer electrolytes for supercapacitors via different industrial application methods

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## ABSTRACT

To date, various types of gel polymer electrolytes have been studied as a potential substitute for liquid electrolytes in energy storage systems, using almost exclusively lab-scale application methods. With a view to scalability and processing time, these methods fail to meet the industrial requirements for fabricating completely printable or coatable supercapacitors. To address the industrial needs, this study investigates the fabrication of a potassium-based gel polymer electrolyte (GPE) layer for an activated carbon supercapacitor via industrial printing and coating methods.

The study examined how a PVA-KOH-based GPE solution can be processed by screen printing and slot-die coating. It proved that the industrial application methods were suitable for coating a GPE layer directly on a supercapacitor electrode as well as for producing free-standing GPE layers. The influence of additives on flow properties was determined via rheological measurements. To evaluate the electrochemical performance, test cells for galvanostatic charge-discharge experiments and impedance spectroscopy measurements were built. It was found that cells containing a GPE layer produced with screen printing and slot-die coating show good cyclability. At a current density of  $2 \text{ mA cm}^{-2}$ , the cells with the slot-die-coated GPE layer reached a specific capacitance of  $87.3 \text{ Fg}^{-1}$  and at  $50 \text{ mA cm}^{-2}$  a specific capacitance of up to  $28.5 \text{ Fg}^{-1}$ . Different layer thicknesses have been realized by varying the parameters of the application methods. The influence of layer thickness on conductivity and specific capacitance was analysed using casted layers. It was found that an optimum exists between the layer thickness of the electrolyte layer and its molar concentration.

## 1. Introduction

With the rise of printed electronics in the past years, the demand for fully printable energy storage systems such as supercapacitors has increased [1,2]. The electronic industry is seeking to use large-scale coating techniques for flexible substrates, such as liquid-film coating or printing, to allow for the cost-efficient production of thin and flexible energy storage systems. In this context supercapacitors based on activated carbon containing aqueous electrolytes like solute potassium hydroxide (KOH) are an eco-friendly, non-inflammable and inexpensive option [3,4]. Today, activated carbon electrodes are generally processed via established industrial coating technologies, enabling economic manufacturing. The separator, however, is a crucial component of the supercapacitor that currently consists of a solid nonwoven fabric. Thus, it cannot be coated or printed but has to be placed in between the electrodes and soaked with electrolyte in additional and complex processing steps.

Hence, the replacement of the separator fabric by a layer serving

both as a separator and an electrolyte is desirable. On the one hand, this layer must effectively prevent the contact between the two electrodes while ensuring a high ion conductivity to enable the electrochemical performance of the cell. Such a layer can be realized by a gel polymer electrolyte (GPE). Generally, GPE systems consist of a liquid phase in which the ions are conducted, incorporated into an insulating polymer host structure. The liquid ion conductive phase can either be an aqueous electrolyte, an organic solvent combined with a conducting salt, or an ionic liquid [5]. The polymer host structure has to provide enough stability to keep the electrodes separated. GPE layers can be fabricated as a thin film out of a polymer solution via various wet chemical processes.

Previous literature reported about dispensing [6] and casting [7] as production techniques for gel electrolytes. However, most of these methods were studied at lab scale [6–10]. Accordingly, the layers produced often have to be dried for several hours. A first approach towards a stencil-printed gel electrolyte based on PAA – which can be photo-polymerized –, for a silver oxide battery has been investigated by

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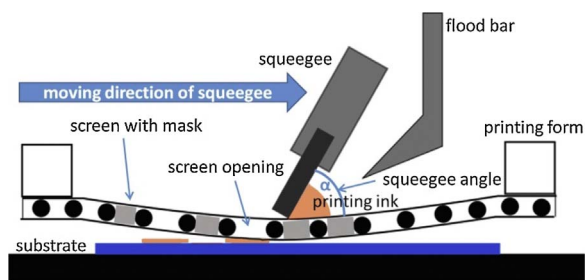


Fig. 1. Working principle of screen printing process.

Braam et al. There a laborious treatment followed the printing of the gel electrolyte to enable an adequate polymerization. Additionally, a re-hydration step was necessary to incorporate sufficient electrolyte solution into the battery [8]. Other approaches involve a complex and time-consuming post-treatment procedure, such as the work described by Barzegar et al. [11] In other studies, the gel electrolyte structure has to be supported additionally by a standard separator layer as described by Kim et al. [12]

None of the preparation methods reported in literature are suitable for large-scale production of fully printed or coated supercapacitors. This paper reports on the production of supercapacitors based on a KOH/PVA electrolyte system by screen-printing and slot-die coating. Those two methods can be used for mass manufacturing either as a sheet-to-sheet process or as a roll-to-roll process, allowing inexpensive large-scale production and any shapes of supercapacitors.

Screen printing is a highly productive method that is commonly used for the precise and structured application of layers (films) containing functional materials [13]. The working principle of screen printing is shown in Fig. 1.

The printing form consists of a fine screen (mesh), on which the printing pattern is left permeable for the printing ink, which contains the functional material. The ink is squeezed through the permeable pattern (openings in the mesh) onto the substrate using a squeegee [14].

Another method to produce functional coatings with defined thicknesses and defined film width at high speed is slot-die coating. The ink is pumped over an inlet into the slot-die unit. Within the slot-die, the dispersion gets pushed into the manifold and is forced to flow through a thin opening restricted by a shim onto the substrate. A meniscus is formed between the slot-die lips and the substrate. This results in a homogeneous film when moving with constant speed over the substrate. The principle of the slot-die process is shown in Fig. 2.

A simple casting method was used to create various thicknesses of free-standing electrolyte layers for a quick evaluation of layer parameters. The selected material system can be easily handled and dried under atmospheric conditions and does not require any post-treatment steps. Since process parameters, e.g. viscosity as well as drying and curing conditions, crucially impact the coating process and hence the

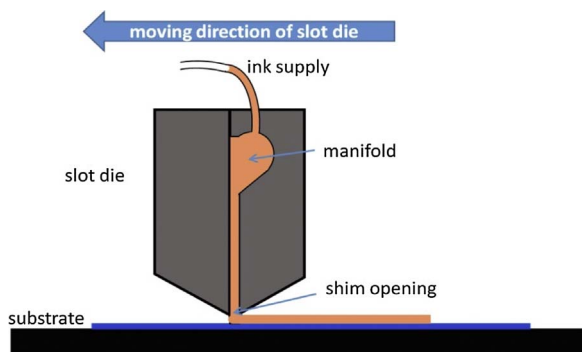


Fig. 2. Working principle of slot-die coating illustration similar to [15].

properties of the resulting layer, those parameters were investigated [16]. Further, the influence of different processing methods on the material's electrochemical behaviour was analysed.

## 2. Material and methods

### 2.1. Preparation of GPE electrolyte solution

In first printing experiments, a GPE recipe based on the work of Saleem et al. [3], containing polyvinyl alcohol, potassium hydroxide (KOH) and water was tested. The GPE solution was prepared by dissolving aqueous potassium hydroxide (KOH) (pellet form, Baker Analyzed™ ACS Reagent, J.T. Baker) in distilled water up to a final concentration of 4.8 M. In a parallel step, polyvinyl alcohol (PVA) (Mowiol 8-88, Kuraray Europe GmbH) with a molar weight of  $67.000 \text{ g mol}^{-1}$  was dispersed with a magnetic stirrer in distilled water. This process requires increased temperatures for 30 min while constantly stirring the solution.

In following experiments the recipe was adapted to prevent bubbles during coating and printing. Therefore 1 wt% of a defoaming agent, either Contraspum Conc. (Zschimmer & Schwarz GmbH & Co KG) or TEGO Airex (Evonik Industries), were added to the PVA solution. The two solutions were mixed by adding the KOH-solution dropwise into the PVA solution while continuously stirring it to obtain a homogenous mixture.

The optimized GPE recipe used for the printing and coating experiments focusing on the influence of layer thickness and drying behaviour consisted of 9.7 wt% PVA 8-88, 11.5 wt% KOH, 77.8 wt% distilled water and 1 wt% Contraspum Conc. additive.

### 2.2. Fabrication of GPE electrolyte layers

Free-standing GPE layers were produced by casting a defined amount of the GPE electrolyte solution ( $V_{es}$ ) into a polyethylene petri dish 53 mm across, resembling an  $A_{Dish}$  of  $0,00221 \text{ m}^2$ . For this method, the wet thickness of the casted layer can be defined by calculating the necessary volume  $V_{es}$  in ml of the electrolyte solution by the formula:

$$V_{es} = \text{wet thickness } (\mu\text{m}) * A_{Dish} (\text{m}^2) = \text{wet thickness } (10^{-6} * \text{m}) * A_{Dish} (\text{m}^2) = \text{m}^3 = 10^6 * \text{ml} \quad (1)$$

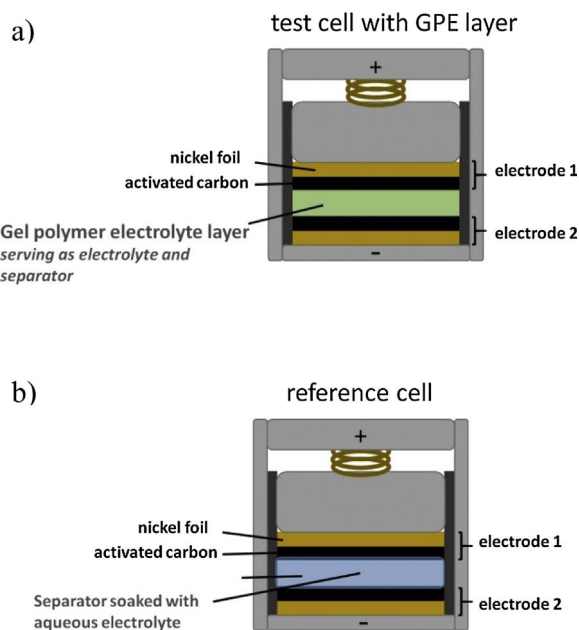


Fig. 3. Test cells for electrochemical measurements a) with GPE layer b) reference cell with liquid electrolyte.

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