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Refilling DSSCs as a method to ensure longevity

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ABSTRACT

Dye-sensitized solar cells can be prepared from non-toxic and inexpensive materials outside a cleanroom and are thus of utmost interest for utilization of different substrates, amongst others on textile fabrics. Since the electrolyte in such cells is usually fluid and the alternatives are mostly toxic, expensive or too rigid to be included in a textile fabric, drying-out of the electrolyte is an urgent problem which must be taken into account. In this study the influence of refilling the electrolyte in different time intervals is investigated, showing that in this way the power reduction with time can be stopped for at least four months. Variations of the maximum power with time depend additionally on the dye used for the cells, showing the least time-dependence for black beans and maqui berry powder, while cells with black rice, exhibiting the largest power after preparation, suffered a severe power drop during this time which could not completely be counteracted by refilling the electrolyte.

1. Introduction

Dye-sensitized solar cells (DSSCs) were developed in 1991 by Michael Grätzel [1]. Since they can be produced from low-cost, non-toxic materials and do not necessitate working in a cleanroom, they can be applied on diverse substrates, e.g. tents or other textile buildings.

In principle, DSSCs work as follows: Dyes typically have energy distances between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in the visible light range. Semiconductors, on the other hand, have band gaps of higher energies, i.e. smaller wavelengths. A typical semiconductor used in DSSCs is TiO_2 in anatase modification with a bandgap of usually 3.2 eV [2]. The LUMO of the dye must have an energy in the conduction band of the semiconductor. Coupling both materials chemically enables electrons from dye molecules, excited by sunlight in the visible range, to be transported through the semiconductor to the anode. Afterwards, the electron is transported through an external load to the cathode and, supported by a catalyst, back into the DSSC. Here it can recombine with an acceptor in the electrolyte which finally reduces the dye cation to its neutral ground state, thus closing the circuit [3–5]. In this way, high conversion efficiencies can be reached, using specialized dyes and nanocrystalline oxide films [6–8]. With purely natural dyes, efficiencies are nowadays limited to approx. 1%, in some cases up to 2–3% [9–12]. With more sophisticated organic dyes, nearly 10% efficiency could be reached [13].

Thinking about using DSSCs on porous substrates, such as textile fabrics, one of the most crucial problems is the drying process of the mostly liquid electrolyte. While semi-solid electrolytes are usually expensive and toxic [14], sealing the electrolyte using wax or resin or embedding it into a polymer coating would result in losing the textile haptics [15,16].

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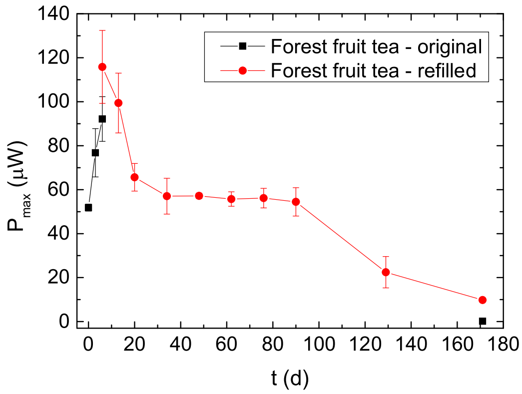

Fig. 1. Test of the influence of refilling a DSSC after different drying periods.

Integration of DSSCs into textile fabrics, however, is an important topic of recent research [17–24], and ideas to solve or avoid this problem are necessary to develop this area of smart textiles further.

This is why in a previous project first tests were performed to examine the possibilities to refill DSSCs either with electrolyte or pure water, showing that refilling with electrolyte was possible after 1 week, but cells kept their significantly reduced efficiency when refilled after 3 months [25]. The investigation reported here gives an overview of the influence of refilling after 1–2 weeks on DSSCs prepared with different natural dyes.

2. Materials and methods

For the DSSCs examined in this study, conductive FTO coated glasses (purchased from Man Solar, The Netherlands) were cleaned and used as cathodes on which graphite was applied using a pencil. Commercially available FTO glasses with an additional TiO_2 coating (Man Solar) were used as anodes to minimize deviations of the semiconducting layer.

Four different dyes were applied which have been shown to work well in DSSCs previously: Black Rice (Badmonkey Botanicals), Black Beans (Badmonkey Botanicals), maqui berry powder (Vitality Nutritionals), and forest fruit tea (purchased from Mayfair). 0.75 g of the powders (or one tea bag in case of forest fruit tea) were mixed with 30 ml water or 15 ml water and 15 ml ethanol, respectively (only in case of maqui berry powder). TiO_2 coated glass plates were left in the dye solution at room temperature for 30 min. Afterwards the excess dye was washed off, and the plates were dried at the air.

Finally, both half cells were put together and fixed using a transparent tape. An electrolyte "type 016" (Man Solar), containing iodine-triiodide, was dropped onto the connection line between both glasses and allowed to spread through the whole cell. This electrolyte has a higher viscosity than usual Lugol's solution and was shown to result in longer lifetime of DSSCs [25].

Refilling was performed in the same way with the same electrolyte at the moments defined in the next section, always waiting 30 min until the corresponding measurement started. Measurements before and after refilling at either day are denoted as "original" and "refilled", respectively.

Measurements were performed using an SMU 2450 SourceMeter (Keithley) in the voltage range from 0.5 V to 0 V, detecting the corresponding currents. A halogen lamp with a color temperature of 3000 K was used to reach a light intensity of 1000 W/m^2 on the cell surface during the measurements.

3. Results and discussion

In a first test, three cells prepared with forest fruit tea were investigated (Fig. 1). After 6 day, the cells were refilled for the first time, showing a clear increase in the maximum power P_{max} measured. The cells were afterwards refilled and measured in periods of 1 week (until day 20) and then in periods of 2 weeks (until day 90). Then, the time intervals were again increased to 40 days. While for refilling the cells each other week, a constant level similar to the initial power could be kept, refilling in intervals of 40 days was apparently insufficient, resulting in a significant decrease of the maximum power. The last measurement, carried out before refilling, resulting in nearly vanishing current and thus negligible power which could only slightly be increased by refilling. Apparently refilling after long durations of drying out does not restore the original properties completely.

In the next test series, three other dyes were used to prepare DSSCs (three specimens each). Since maqui berry powder had shown in previous experiments to reach higher efficiencies when dissolved in a mixture of water and ethanol instead of pure water, an additional set of three samples was prepared using this solvent. Time intervals between two refilling steps were varied between 3 days and 2 weeks, the latter being the longest interval used in the first experiment which resulted in restoration of the last power.