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UV-crosslinked polymer electrolyte membranes for quasi-solid dye-sensitized solar cells with excellent efficiency and durability

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Supporting information

Summary

1) Screening DoE

The two-level fractional factorial design (resolution V) is a screening-type design of experiments useful to eliminate unimportant factors. The five factors selected in this study are shown in Table S1, together with their relative experimental domain.

Table S1: Factors and experimental domain selected for the two-level fractional factorial design (resolution V).

Factors	Experimental domain
BEMA:PEGMA ratio	0-100 to 100-0 wt%
NaI concentration	0.15 to 1.0 M [NaI : I_2 = 10 : 1 mol/mol]
$LiClO_4$ concentration	0 to 0.5 M
Propylene carbonate concentration	0 to 20 wt%
Swelling time	5 to 50 min

20 experiments were carried out in this experimental domain. The model was evaluated through analysis of variance (ANOVA). Its regression coefficient (R^2) of 0.948 is in reasonable agreement with the experimental results, indicating that 94.8% of the variability can be revealed by the model and 5.2% residual variability remains.

Fitted coefficients of the chemometric model are reported in Table S2. Due to their low influence on the experimental response (light-to-electricity conversion efficiency), the three factors *$LiClO_4$ concentration*, *Propylene carbonate concentration* and *Swelling time* can be assumed irrelevant and will not be considered in future experiments. For these latter, a swelling time of 5 min has been chosen as optimum as an extended swelling did not reflect on the ionic conductivity of the polymer electrolyte membranes.

Table S2: Model coefficients of the two-level fractional factorial design (resolution V).

Factors	Coefficients
BEMA:PEGMA ratio	1.07 +/- 0.06
NaI concentration	1.79 +/- 0.09
$LiClO_4$ concentration	0.14 +/- 0.02
Propylene carbonate concentration	-0.11 +/- 0.02
Swelling time	0.06 +/- 0.01
Constant term	2.14 +/- 0.10

2) Kinetics study

The kinetics of the photo-polymerization process was investigated by using FT-IR spectroscopy (NICOLET-5700 FT-IR instrument by Thermo Fisher Scientific Inc., Illkirch, France) which collects the spectra in real time while the sample is irradiated by UV light, following the decrease in the area of the band attributable to the methacrylate groups at 1630 cm^{-1}. The tests were carried out at ambient temperature on a UV transparent SiC wafer. A medium pressure mercury lamp (Hamamatsu) equipped with an optical guide was used to induce photo-polymerization (light intensity on the surface of the sample: 30 mW cm^{-2}).

Fig. S1 shows the percentage of conversion of the BEMA-PEGMA reactive mixture under UV light as a function of the irradiation time. The reactivity of all the monomers was very high in the initial stages of UV-curing, the rate of polymerization was very fast and the conversion was completed in less than 300 s.

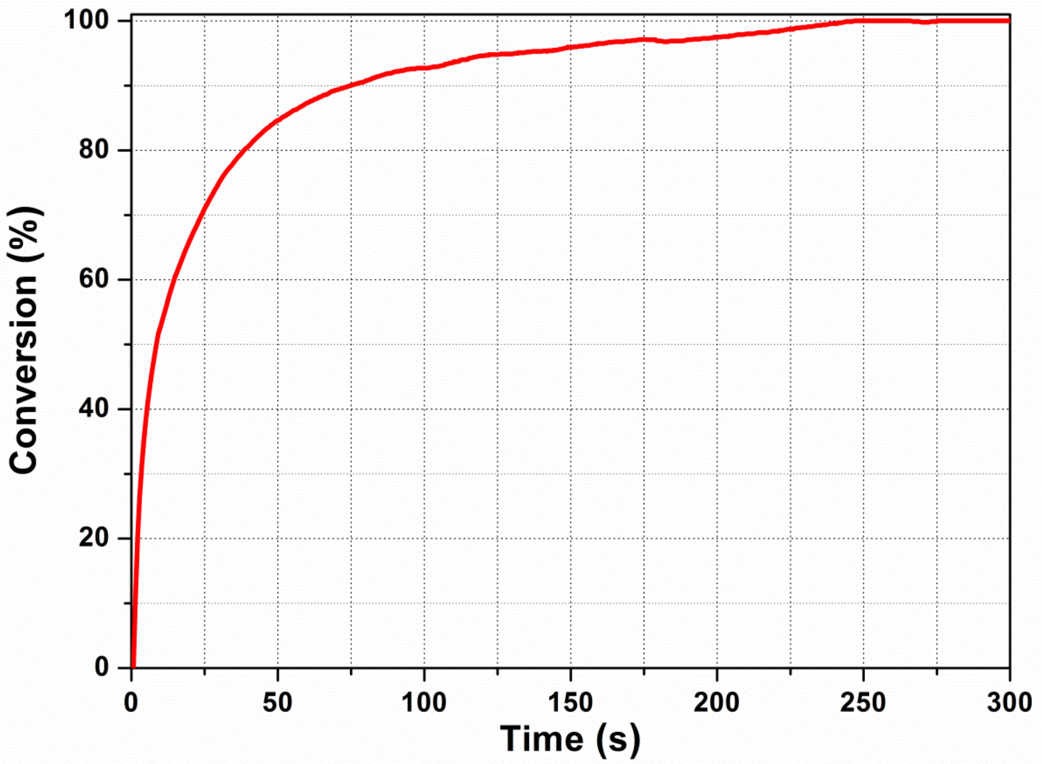

Fig. S1 Methacrylic double bonds conversion of the reactive monomer mixtures checked by real-time FT-IR spectroscopy as a function of the irradiation time.

3) Thermogravimetric analysis

The thermal stability of the different polymer membranes was assessed by thermogravimetric analysis (TGA) and the resulting thermograms are reported in Fig. S2. Analyses were performed in the temperature range 25-500 °C using a TGA/SDTA-851 instrument (METTLER, Zurich, Switzerland) under N_2 flux at a heating rate of 10 °C min^{-1}.

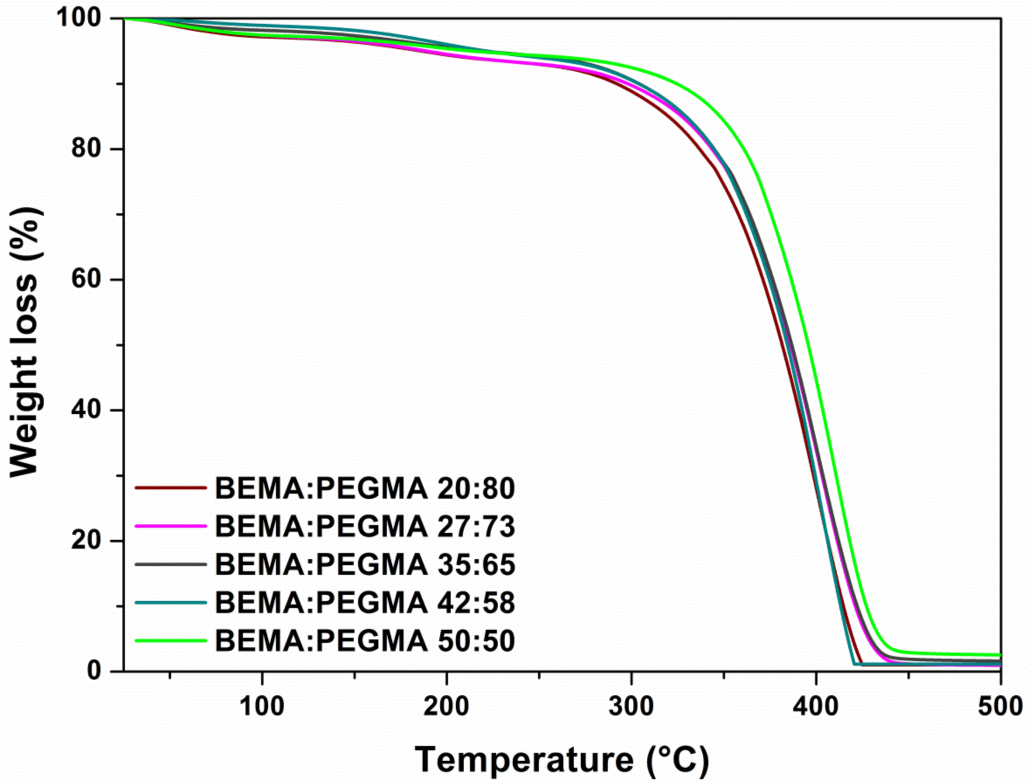

Fig. S2 TGA analysis under N_2 flux (temperature range 25-500 °C) of BEMA:PEGMA polymer membranes before swelling in the liquid electrolyte solution.

The thermal stability of the BEMA-PEGMA membranes was found to be very high if one considers that, generally, the operating temperature of DSSCs does not exceed 65-70 °C. The activated polymer membranes (after swelling in liquid electrolyte) were also tested for their thermal stability. Even though the liquid electrolyte addition reduced the thermal stability up to approx. 82 °C, which is the temperature at which the solvents began to evaporate, this is well in the limit of applications as electrolyte for DSSC devices.

4) Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements were performed in order to study the transport and recombination mechanisms of the liquid electrolyte- and quasi-solid-based cells. The spectra were collected in dark condition using a CH Instruments 760D electrochemical workstation in the frequency range between 10 mHz and 20 kHz, varying the applied bias voltage (the amplitude of the AC signal was 10 mV). The experimental curves were fitted using an equivalent circuit.[1] There, the resistance R_s represents the contact series resistance, the electrolyte-photoanode interface is modeled by the parallel $R_1//Q_1$, the parallel $R_2//Q_2$ stands for the electrolyte-counter electrode interface and the Warburg element W models the diffusion into the electrolyte. Q_1 and Q_2 are constant phase elements (CPEs) that are a generalization of common capacitances introduced to

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[1] A. Sacco, A. Lamberti, D. Pugliese, A. Chiodoni, N. Shahzad, S. Bianco, M. Quaglio, R. Gazia, E. Tresso, C. F. Pirri, *Appl. Phys. A - Mater. Sci. Process.*, in press, doi: 10.1007/s00339-012-7268-9.

account some frequency dispersion present in the impedance spectra.[2] The EIS curves measured at open circuit voltage for the two different cells immediately after fabrication and upon storage at 60 °C (for 90 h or 240 h) are reported in figure S3, together with the results of the fitting.

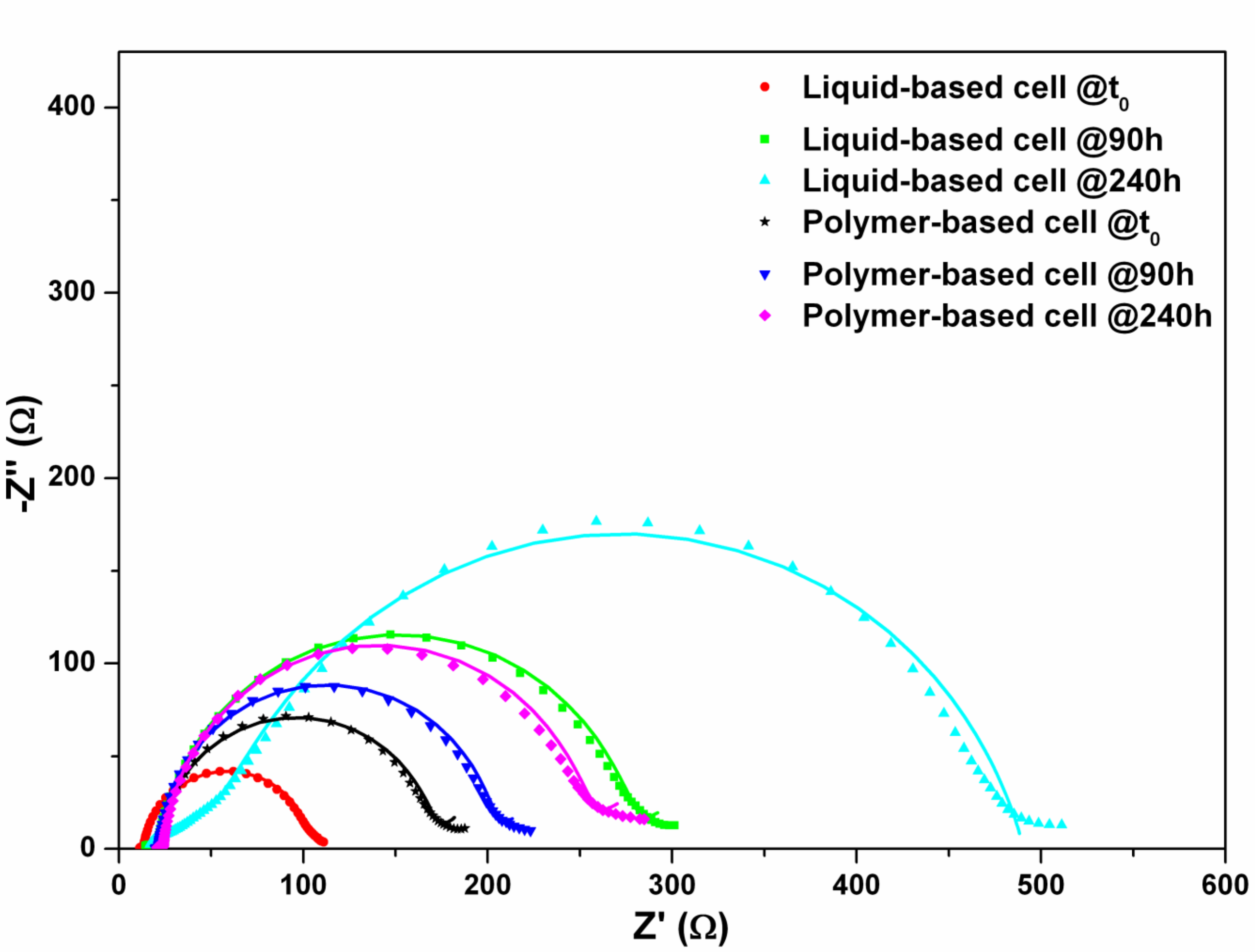

Fig. S3 Measured (symbols) and fitted (solid lines) impedance spectra at open circuit voltage of DSSCs fabricated with polymer electrolyte membrane and liquid electrolyte. For each cell, the spectrum of the fresh-assembled device and the spectra measured after 90 h and 240 h of storage at 60 °C are reported.

From the fitting parameters, we calculated the chemical capacitance values C_μ by using the formula:

$$C_\mu = Q_1^{\frac{1}{\beta_1}} R_1^{\frac{1}{\beta_1}-1}$$

where β_1 is the exponent of CPE Q_1.
In Figure S4 the chemical capacitance values as a function of the bias voltage are shown. The typical exponential dependence on the applied voltage is evident in the semi-logarithmic plots. It can clearly be seen that the liquid electrolyte-based cell presents chemical capacitance values that decrease upon time, while these values remain almost constant for the polymer-based cell, evidencing its remarkably increased long-term stability, due to higher electron injection.

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[2] J. R. Macdonald, *Ann. Biomed. Eng.* 20 (1992) 289-305.

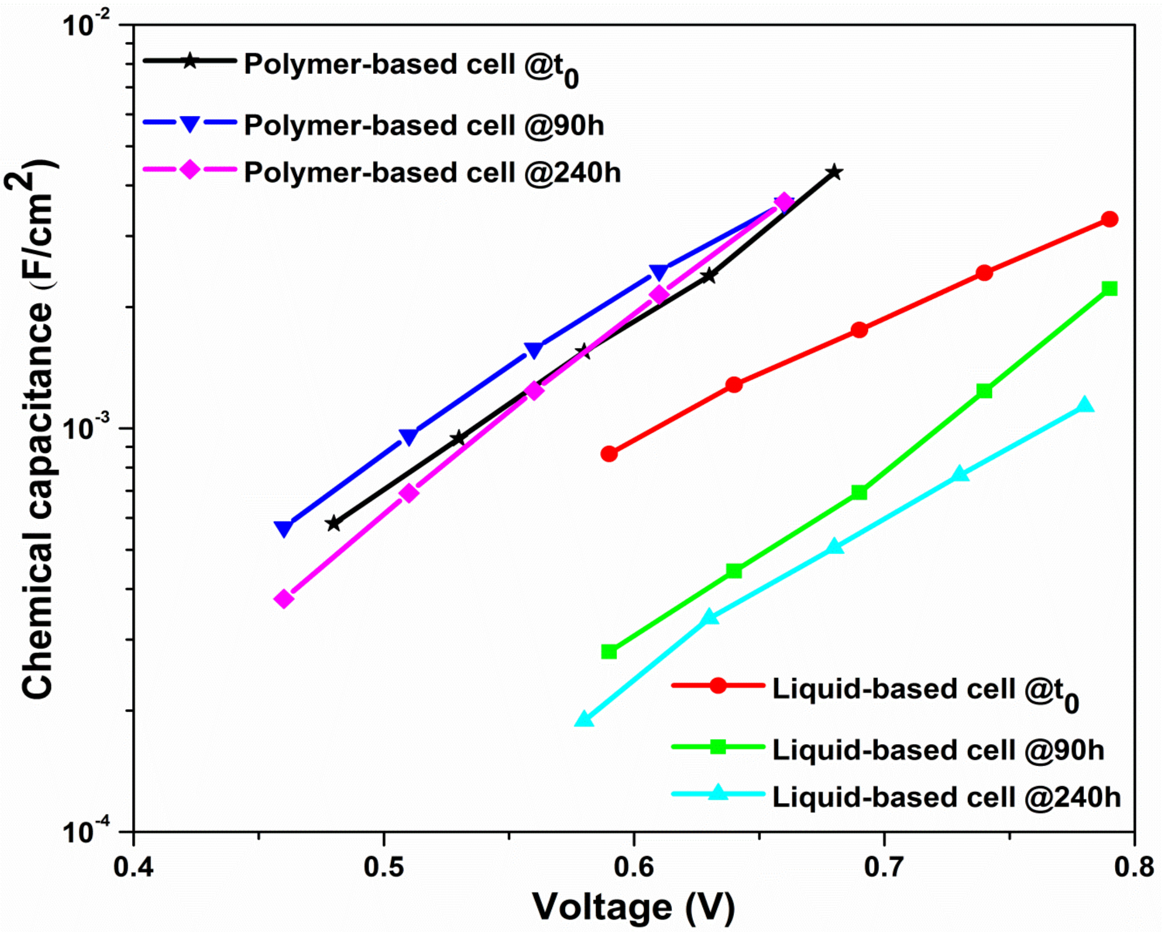

Fig. S4 Chemical capacitance dependence on the bias voltage for DSSCs fabricated with polymer electrolyte membrane and liquid electrolyte. For each cell, the curves related to the fresh-assembled device and to the cells after 90 h and 240 h of storage at 60 °C are reported.

5) Emission spectrum of the UV-lamp

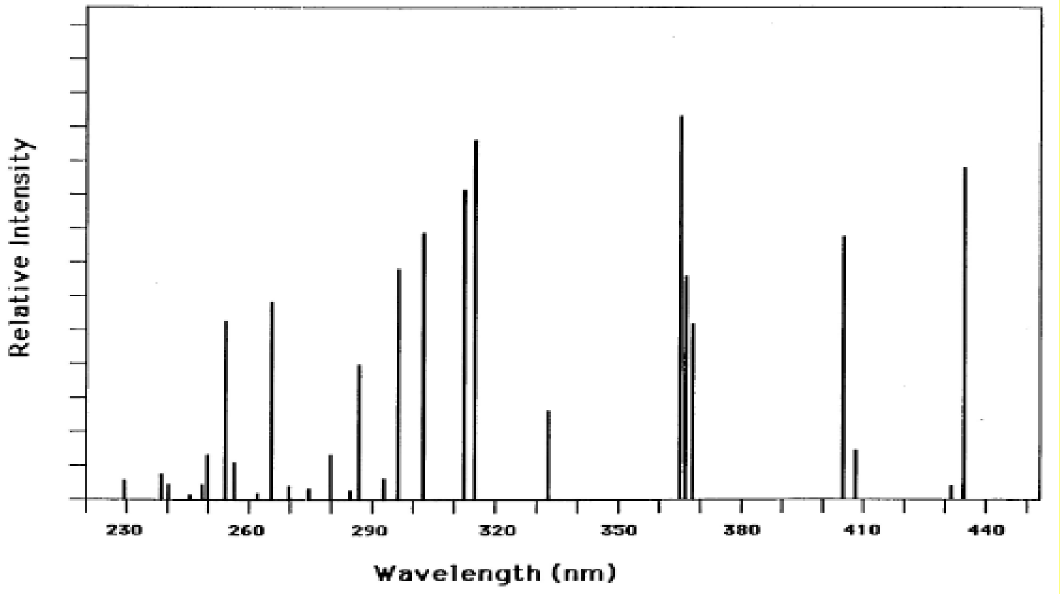

Fig. S5 Emission spectrum of the medium vapor pressure Hg lamp used to carry out the photo-polymerization.