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Theoretical analysis and characterization of the energy conversion and storage efficiency of photo-supercapacitors

Balthazar Pierre Lechene[a], Raphael Clerc[b], Ana Claudia Arias[a,*]

[a] Department of Electrical Engineering and Computer Sciences, University of California, Berkeley, CA 94720, USA

[b] Université de Lyon, UJM-Saint-Etienne, Institut d'Optique Graduate School, CNRS, UMR5516, Laboratoire Hubert Curien, F-42023, Saint-Etienne, France

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ABSTRACT

The time-dependent dynamics of the charge and discharge of photo-supercapacitors (PSC), devices which combine a supercapacitor with a solar cell, are investigated using a semi-analytical model. For a given PSC, it is found that the maximum Energy Conversion and Storage Efficiency (ECSE) is a direct function of the Power Conversion Efficiency (PCE) and Fill Factor (FF) of the solar cell. The capacitance, series and shunt resistances of the supercapacitor affect the time constants of the PSC and the value of the maximum ECSE. To experimentally measure the maximum value of ECSE with at most 2 charge-discharge cycles, a simple experimental procedure is proposed, which consists in comparing the power flowing through the supercapacitor and the energy already stored in it. The theoretical results are validated with experiments on a PSC made from an organic solar cell and a commercial supercapacitor.

1. Introduction

Photo-supercapacitors (PSC) are devices combining solar cells with supercapacitors in order to simultaneously generate and store energy from light. They can be particularly useful as independent energy sources to power autonomous devices such as wearables and Internet of Things nodes [1–3], or to act as buffers to mitigate the effects of solar light fluctuations on energy generation [4,5]. One of the main advantages of PSC is their simplicity (only two elements), as they do not need interfacing electronics between the solar cell and the supercapacitor, thus offering a lot of flexibility in their design and fabrication [6]. PSC can be fabricated as a single stack where the generation and storage components share a common electrode, which considerably reduces resistive losses and minimizes footprint [7]. They can also be fabricated in specific formats, like a fiber [8], or using low-cost solution processing techniques compatible with flexible substrates [1,2,9].

A typical figure of merit of PSC is the energy conversion and storage efficiency (ECSE) over a complete charge-discharge cycle, sometimes also called "overall efficiency" [5,10] or "photoelectric conversion and storage efficiency" [8,11]. The ECSE of a PSC is measured by performing a charge-discharge experiment: during the charging phase, the solar cell is exposed to light, which charges the initially empty supercapacitor. After a certain amount of time, the charging is stopped and the supercapacitor is discharged, either at constant current [12] or into a given load [13]. The ECSE is then defined as the ratio of electrical energy discharged from the super-capacitor over the light energy received by the solar cell during the charging period.

The duration of the charging phase and the incident light power influence the measured ECSE value of a PSC: as the supercapacitor is charging, its voltage increases, which modifies the output power of the solar cell over time [9,12]. For a given light power, each system thus displays a maximum ECSE value. In order to identify this maximum, multiple charge-discharge experiments must be performed, each with a different charging time, which can be problematic if the solar cell's efficiency changes during the prolonged light exposure. While the maximum ECSE of a PSC cannot be higher than its solar cell's power conversion efficiency (PCE), the relation between the two can vary widely: in previous work [10,11,14–16], the ratio ECSE/PCE can go as low as 0.12 [16] and as high as 0.81 [15].

In this work, we develop a theoretical model to investigate how the performance of a PSC relates to the characteristics of its solar cell and supercapacitor, and we demonstrate an experimental method to identify and reliably measure the maximum ECSE in a simple way. The model describes the temporal evolution of a PSC during charge and identifies how it is influenced by the solar cell's J-V characteristic and by the supercapacitor's capacitance and parasitic resistances (shunt and series). It is found that the theoretical maximum ECSE depends only on the solar cell's PCE and its Fill Factor (FF), while the supercapacitor's shunt and series resistances can lower the effective ECSE under this theoretical value. The supercapacitor's capacitance mostly influences

* Corresponding author.
E-mail address: acarias@berkeley.edu (A.C. Arias).

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the time at which the maximum ECSE occurs. Moreover, the theoretical value of the solar cell's voltage upon occurrence of the maximum ECSE is determined to be solely a function of the FF and the V_{oc} of the solar cell. Based on the theoretical analysis, a method is proposed to experimentally determine the charging time yielding the maximum ECSE of a PSC, with at most two charge-discharge cycles. This method involves following in real time the power flowing to the supercapacitor and the corresponding stored energy and does not require prior knowledge of the capacitance of the supercapacitor. These results are validated by comparing charge-discharge experiments and simulations of an actual PSC made of an organic solar cell and a commercial supercapacitor.

2. Experimental methods

2.1. Solar cell fabrication

The solar cell fabrication was taken from ref. [9]. ITO-covered glass (from Thin Film Devices) were sequentially cleaned in acetone, isopropanol and water, then passed under UV-ozone plasma treatment for 30 min. PEDOT:PSS (Heraeus Clevios VPAI 4083, 40 nm) was spin-coated and baked at 180 °C for 10 min. After transfer in a glovebox, a PCDTBT:PC_{71}BM (1:3.7 in ortho-dichlorobenzene with 5% dimethyl sulfoxide) solution was spin-coated above (80 nm). PCDTBT was purchased from Saint-Jean Photochimie and PC_{71}BM from Solaris. Finally, PEIE (Sigma Aldrich) diluted to 0.048 wt% in ethanol was also spin-coated and the whole device was annealed at 70 °C for 10 min. 200 nm of aluminum were thermally evaporated to complete the devices.

2.2. Electrical characterization

The solar cells' J-V curves were acquired using a Keithley 2400. For PSC characterization, current and voltage measurements in part 4 were obtained using two synchronized Keithley 2400. For the sun spectrum, a solar simulator from Newport Oriel Sol1A (xenon lamp). The power was calibrated with a Newport System V reference silicon solar cell.

3. Theory and calculations

3.1. Electrical circuit and equations

For the purpose of this theoretical study, the solar cell – supercapacitor system is represented as a circuit comprising a solar cell, an ideal capacitor of capacitance C (which can be assumed voltage dependent or not, as discussed later), a series resistance R_s, and a shunt resistance R_{sh}, as shown in Fig. 1a. V_{pv} is the voltage across the solar cell, I is the current generated by the solar cell, V_{Rs} is the voltage across the series resistance and V_{capa} is the voltage across the supercapacitor and the shunt resistance. The current flowing through the supercapacitor is i_c. In this model, the solar cell's voltage V_{pv}, and current I (V_{pv}), are related together by the solar cell's I-V characteristic. The non-idealities of the solar cell are taken into account by its I-V characteristic through the variation of its apparent Fill Factor F. The shunt and series resistances of the circuit correspond in fact to the capacitor's internal equivalent series resistance (ESR) and shunt resistance.

Solar cells I-V characteristics are usually modeled by the Shockley diode equation. However, when accounting for internal resistances, the current becomes a self-consistent function of itself, making this expression difficult to deal with mathematically. Therefore, in this work, the solar cell's I-V characteristic is modeled with an empirical elliptic equation:

$$I(V) = I_{sc}\frac{V_0}{V_{oc}}\frac{V - V_{oc}}{V - V_0} \tag{1}$$

where V_{oc} is the open circuit voltage of the solar cell and I_{sc} its short-circuit current. This equation fulfills the requirement $I(0) = I_{sc}$ and $I(V_{oc}) = 0$. V_0 is a parameter (necessarily greater than V_{oc}) related to the Fill Factor and is representative of the solar cell's internal parasitic resistances. It can be shown that:

$$V_0 = V_{oc}\left[\frac{2\sqrt{F^3} + F}{4F-1}\right] = V_{oc}f(F) \tag{2}$$

where F is the Fill Factor and f(F) represents the function in the brackets. A Fill Factor F = 0.5 leads to a ratio V_0/V_{oc} equal to 1.2, whereas if F = 0.8, V_0/V_{oc} = 1.01. (Note that in this model, the minimal value of F is limited to 0.25, which is not really an issue as the Fill Factors of solar cells are typically higher). Fig. 1b shows I-V curves generated with this equation for V_{oc} = 0.9 V, I_{sc} = 12 mA and F varying from 25% to 80%. Compared to the Shockley diode equation, the main drawback of this expression of I-V is that the relative influence of the solar cell's series or shunt resistances on the Fill Factor is no longer explicit and thus cannot be specifically addressed. Still, this elliptic representation of I-V characteristics allows to realistically model a solar cell's overall electrical behavior, allowing to easily vary its Fill Factor, V_{oc} and I_{sc}, while being integrable and differentiable.

The voltage and current parameters of the circuit of Fig. 1a follow the differential equation:

$$C\frac{dV_{capa}}{dt} = I(V_{pv}) - \frac{V_{capa}}{R_{sh}} \tag{3}$$

Which can be re-written as a function of V_{pv} solely using $V_{capa} = V_{pv} - R_s I(V_{pv})$:

$$C\frac{dV_{pv}}{dt}\left(1-R_s\frac{dI(V_{pv})}{dV_{pv}}\right) = I(V_{pv}) - \frac{1}{R_{sh}}(V_{pv} - R_s I(V_{pv})) \tag{4}$$

If there are no series or shunt resistance (ideal supercapacitor), the equation reduces to the form below:

$$C\frac{dV}{dt} = I(V) \tag{5}$$

where $V = V_{pv} = V_{capa}$. Both differential Eqs. (4) and (5) are non-linear and thus in principle difficult to solve. However, thanks to the elliptical expression of I(V) of Eq. (1), the simplified Eq. (5) can be analytically solved, as shown in Section 4.1. When series and shunt resistances are taken into account, a closed-form solution of the differential Eq. (4) can no longer be found. Eq. (4) is thus simply integrated numerically, avoiding time consuming numerical techniques usually employed to solve differential equations (such as Runge Kutta for instance) and their related potential stability issues. To do so, the differential Eq. (4) is re-written as:

$$C\frac{\left(1-R_s\frac{dI(V_{pv})}{dV_{pv}}\right)}{I(V_{pv}) - \frac{1}{R_{sh}}(V_{pv} - RsI(V_{pv}))}dV_{pv} = dt \tag{6}$$

By calling $A(V_{pv})$ the left end side term, the circuit's time evolution can be determined by numerically integrating Eq. (7) for every value of voltage V_{pv} ranging from $V_{pv}(t = 0)$ to V_{oc}:

$$\int_{V_{pv}(t=0)}^{V_{pv}} A(v)dv = \int_0^{t(V_{pv})} dt = t(V_{pv}) \tag{7}$$

The time $t(V_{pv})$ is the time it takes for the system to reach a voltage across the solar cell equal to the value V_{pv}. From the value of V_{pv} and the elliptical expression of $I(V_{pv})$, it is possible to deduce the value of all the circuit's parameters: V_{capa}, i_c, the quantity of charges and energy stored in the supercapacitor. The system's charge is always considered to start from a completely empty supercapacitor ($V_{capa}(t = 0) = 0$). Therefore, the starting voltage for the integral calculation is determined by the initial condition: $V_{pv}(t = 0) = Rs\,I(V_{pv}(t = 0))$.