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Determination of the intrinsic diode parameters of polymer solar cells

L.H. Slooff*, B. Brockholz, W.J.H. Verhees, S.C. Veenstra, E.M. Cobussen-Pool, J.M. Kroon and E.E. Bende

Energy research Center of the Netherlands, Solar Energy, PO Box 1, 1755 ZG Petten, The Netherlands

Abstract

Polymer solar cells offer a promising low cost alternative in photovoltaics if the expensive ITO electrode can be omitted. Recently an alternative based on highly conductive PEDOT:PSS in combination with current collecting grids was developed.[1] Electrical modeling is carried out to optimize the grid pattern in these polymer solar cells. The basic inputs for this type of modeling are the resistivity of the materials, film thicknesses and the diode parameters of the solar cell. The diode parameters are often determined by fitting the experimental current-voltage measurements to a one-diode model. This gives the well-known dark saturation current density (J_0), diode ideality factor (n), photocurrent density (J_L), shunt resistance and series resistance. However, the fitted parameters do not always correspond with the intrinsic solar cell parameters, i.e. those that correspond to an infinitesimally small diode, but they are actually lumped parameters containing information of the heterogeneity of the system. For this reason, two one-diode fits corresponding to two different systems (in size and geometry) can yield different intrinsic diode parameters. The reason for this can be found in the heterogeneity of the system.

We show an approach to determine the so-called intrinsic diode parameters, by fitting the experimental IV curve against a simulated IV curve that is obtained from a model in which the experimental solar cells are explicitly modeled in 3D.

This model provides a simple basis to determine the intrinsic solar cell parameters that can be used for the optimization of grid patterns for polymer solar cells.

Keywords: polymer photovoltaics; modelling

* Corresponding author. E-mail address: slooff@ecn.nl

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1. Introduction

Modeling of solar cells is a powerful tool in the optimization of cell performance. Various reports have been written on the optimization of solar cells.[2-5]Among them a few can be found on optimization of polymer solar cells in particular.[6] In most cases the optimization is done using input parameters like the diode parameters and sheet resistances of the materials in the cell. In those cases, the result strongly depends on the accuracy of these input parameters. Often the diode parameters are obtained by fitting a 1-diode model to experimental data or a measured current and voltage at maximum power point is used. However, in these parameters also the device lay-out plays a role and it only gives the correct diode parameters if the cell is infinitesimally small, not measured using an illumination or aperture area mask[7] and if the series resistance in the cell is very small. More often the fitted parameters are actually lumped parameters containing information of the heterogeneity of the total system. Firstly, the distributed series resistance effect results in a voltage distribution across the solar cell in the lateral direction, which causes that all notional diodes operate at different voltages. Secondly, aperture area masks are used when accurate IV measurements of organic solar cells are carried out. In that case, the intrinsic diode parameters may differ for the illuminated and shaded areas and, moreover, the shaded area will deprive current from the illuminated zone, resulting in lower open-circuit voltages.

Although there are discussions on whether organic solar cells can be described with a 1-diode equation, several groups have reported on fitting of organic solar cells using an (adapted) 1-diode model.[8-11] We will show a simpler approach, based on the standard 1-diode equation, to determine the so-called intrinsic solar cell parameters, i.e. without the influence of the contacts. This is done by simultaneously fitting simulated I-V curves from a 3D finite element model to the experimental data of cells with different geometries. These intrinsic solar cell parameters can then be used for optimization of grid patterns for cells and modules.

2. Models

In electrical optimization of solar cells, the diode parameters of the solar cell without the resistance influence of the contacts must be used, i.e. the intrinsic diode parameters. Most of the time current-voltage experiments are fitted with a one-diode model to obtain the diode parameters and the series resistance of the cell. This gives the well-known dark saturation current density (J_0), diode ideality factor (n), photocurrent density (J_L), shunt resistance and series resistance. However, the fitted parameters do not always correspond with the intrinsic solar cell parameters, but they are actually lumped parameters containing information of the heterogeneity of the system. For small cell sizes and/or cells with a small series resistance, this one-diode model with lumped series resistance can be used. Cells with a high series resistance must be modeled with a one-diode model with distributed series resistance, which needs a finite element method (FEM).

2.1. One-diode model with lumped series resistance

In the one-diode model with lumped series resistance it is assumed that each part of the cell experiences the same voltage, see Fig.1. This is only true if the cell is infinitesimally small or has a very small series resistance. As a result, a fit to the diode equation (Eq. 1) gives only correct 'intrisic' cell parameters for very small cells and cells with a very small series resistance.

$$J(V) = J_{ph} - J_0\left(e^{\frac{q(V-R_sJ)}{n \cdot kT}} - 1\right) - \frac{V - R_sJ}{R_{sh}} \qquad (1)$$

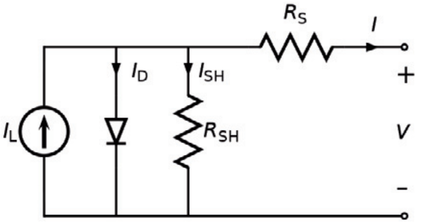

Fig. 1. Replacement scheme of solar cell with lumped series resistance (Rs). This electronic circuit also shows the photon current (I_L), the dark saturation current (I_D) and the shunt resistance (R_{SH})

2.2. One-diode model with distributed series resistance

For cells with a large series resistance, the operating voltage changes in the lateral direction over the cell. As a result, each part of the cell operates at a different voltage, depicted in Fig. 2. This can be calculated using a finite element model (FEM), which calculates the operating voltage of the diode at each nodal point over a mesh. In this work we used the FEM program Abaqus.

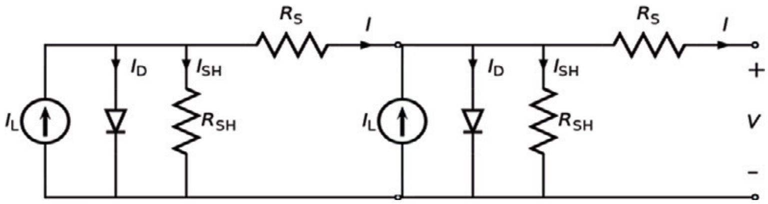

Fig. 2. Replacement scheme of solar cell with distributed series resistance

3. Experimental

3.1. Preparation

Glass substrates of 3x3 cm^2 were used with pre-patterned ITO electrodes (Naranjo substrates). The substrates were carefully cleaned, dried, and treated with UV/O_3 prior to use. On the substrates, a 40 nm thick layer of PEDOT:PSS (Clevios Al 4083, H.C. Starck) was spin coated. Samples were subsequently dried for 10 minutes at 120°C.

A P3HT:[C60]PCBM blend was used as the photoactive layer deposited by spin coating an ortho-dichlorobenzene solution containing the P3HT (Plexcore OS2100, Plextronics):[C60]PCBM (99.5%, Solenne B.V.) mixture in a weight ratio of 1:1 (2.0 wt % for both P3HT and [C60]PCBM). The spin-coating conditions were adjusted to give photoactive layers with the desired thickness. Samples were annealed at 120°C for 5-10 min.

The devices were completed by vacuum deposition of the counter electrode. The counter electrode consists of a 1 nm layer of LiF and 80 nm of Al. The electrode layers were vacuum deposited at 1×10^{-6} mbar through a shadow mask. In this way, 4 cells were obtained with active areas of 0.10 cm^2, 0.17 cm^2, 0.37 cm^2, and 1.0 cm^2 on the same substrate, see Fig. 3.

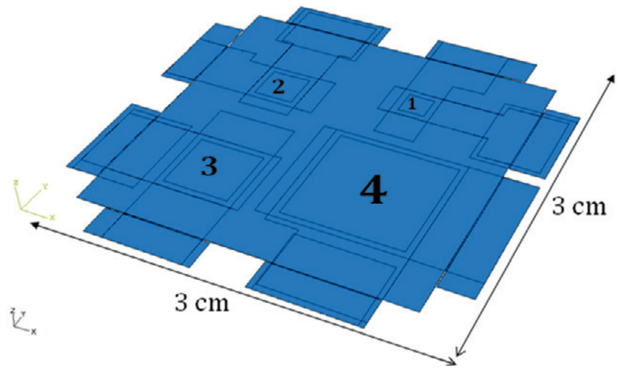

Fig. 3. Drawing of the device layout as used in the experiment.

3.2. Characterization

Film thickness measurements were performed with a Dektak 8 surface profilometer (Veeco). Current-voltage (I/V) measurements were done in a setup (MiniSunSim) of home-made design, containing a Keithley 2400 SourceMeter wired to a sample holder in a nitrogen-filled glove box. The sample was illuminated by a halogen lamp. An automated rotating filter wheel was used to record the current densities at various wavelengths for external quantum efficiency (EQE) measurement. A silicon reference cell with known spectral response was used for calibration purposes. This enabled the measurement program on the computer to calculate an estimation of the short-circuit current of the organic solar cell under 1000 W/m^2, AM1.5 illumination ($J_{sc,SR}$). Using this calculated short circuit current we estimated the power conversion efficiency (PCE) by: $PCE = V_{oc}$ (V) $*FF*$ $J_{sc,SR}$ (mA/cm^2). This is only a valid approach if the current is linear with illumination intensity. For most measurements, the calculated short circuit current from the EQE measurement was within 10% of the short circuit current measured under the solar simulator.

For standard test condition (STC) measurements, a WXS-300S-50 solar simulator (WACOM Electric Co.) was used. The mismatch factor (for these measurements, 0.96< mismatch factor <1) was calculated using a recent spectrum of the simulator lamp and the spectral responses of the used filtered Si reference cell (calibrated at the Fraunhofer ISE, Freiburg) and the polymer:fullerene cell, respectively.

Samples were illuminated through an illumination mask with a specific aperture area, as indicated by the inner squares around the cell numbers in Fig. 3.

4. Results

4.1. Lumped series resistance

Current voltage measurements were performed on all 4 cells in the dark and under illumination as described above. The resulting I-V curves under illumination are shown in Fig. 4, where the current was normalized to the short circuit current. The cell numbers indicated in the legend correspond to the numbers in Fig. 3.

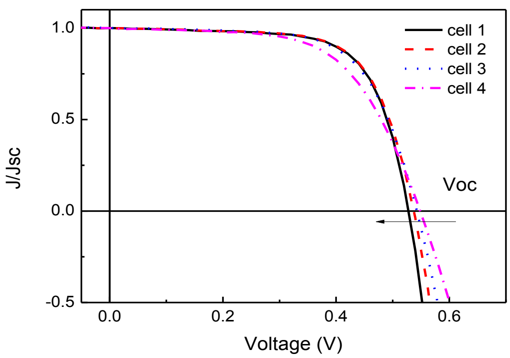

Fig. 4. Normalised I-V characteristics of 4 polymer PV cells of increasing size. The cell numbers correspond to those of Fig. 3.

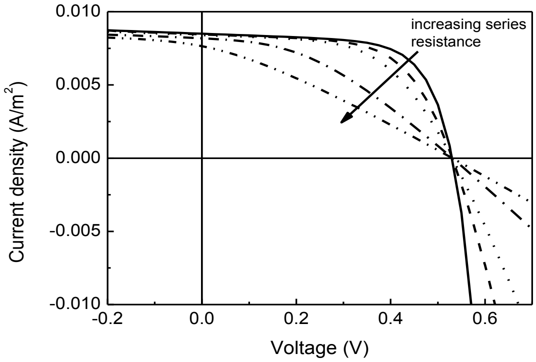

Fig. 5. Effect of increasing series resistance on the shape of an I-V curve

Fig. 5 shows that the fill factor decreases with increasing cell size, which can be attributed to an increasing series resistance. However, the open-circuit voltage is by definition not affected by the series resistance, since no current flows. The decreasing Voc with decreasing cell size must therefore have another cause.

Quite commonly I-V curves are fitted using a one-diode model with a lumped series resistance. As reference, all experimental IV curves of the four cells were simultaneously fitted with a one-diode model assuming lumped series resistance. As all cells are made on the same substrate, it was assumed that they have similar diode characteristics and only the series resistance changed from cell to cell due to the different contact area. The experimental data and fit are shown in Fig. 6.

From this figure it can be seen that the fits are rather good around short circuit conditions, but around the maximum power point (MPP) and beyond, the fits from cell 1 and 4 deviate substantially from the experimental data. This shows that the 1-diode model with lumped series resistance is not accurate enough for fitting these polymer solar cells.

There are three possible reasons for the discrepancy.

1. A lumped series resistance model was used, but the cells might already have a too high series resistance to fulfill the assumption of a constant operating voltage over the whole cell.
2. An illumination mask is used, which causes part of the cell to operate in the dark.
3. The cells show different diode properties under illumination and in the dark as was reported earlier for polymer solar cells.[12]

Below we describe all three phenomena to see if and how they affect the I-V curves.

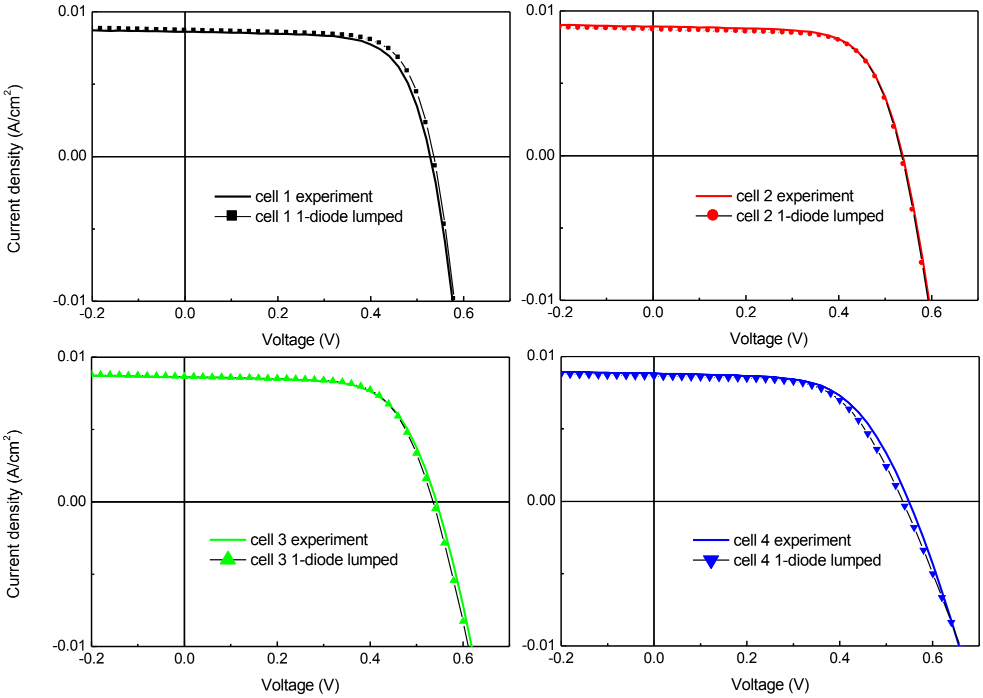

Fig. 6. Experimental I-V curves for all four cells plotted with a fit to a 1-diode model with lumped series resistance.

4.2. Distributed series resistance

A one-diode model with a distributed series resistance was implemented by building the sample with four cells in the FEM program Abaqus. First, only the illuminated part of the active layer was taken into account to simulate the previous fit from paragraph 4.1, i.e. a 1-diode model on the illuminated active area, but now considering also the distributed series resistance. The same set of materials and diode parameters as in the fit of the lumped series resistance were put into the model. The result is shown in Fig.7 cell 4 (largest cell) together with the fit of the lumped series resistance model. As can be seen, there is a perfect match between the model with lumped series resistance and distributed series resistance, showing that in this experiment (size of 0.81 cm^2) the distributed series resistance does not play a role.

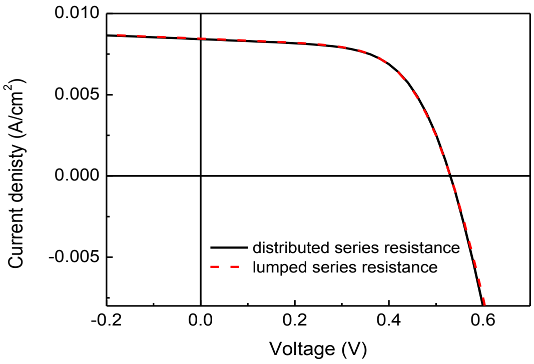

Fig. 7. Comparison between a lumped resistance and a distributed resistance model.

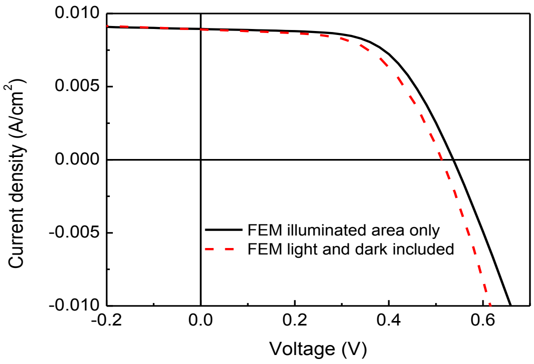

Fig. 8. FEM with only the illuminated part taken into account and a FEM model with the whole cell, i.e. light and dark part, taken into account

Second, the dark part of the active layer was added to the model, simulating the real experimental situation, maintaining the same material and diode parameters as in the previous models. So the dark and illuminated part had the same parameters except for the photocurrent. The result is shown for cell 4 in Fig.8. Clearly, the contribution of the dark part results in strong deviations from the model that only took the illuminated part into account. This shows that a fit to the data does not give the correct parameters for the illuminated diode when an illumination mask is used, as the dark part has a large contribution to the I-V curve. The fit in Fig.6. showed that the deviation with the experiment was mainly around maximum power point, but the curve in Fig.8. with the light and dark part included differs in the whole range for V>0V. This shows that even using a model that includes the dark area will not result in a correct fit to the experimental data of these polymer solar cells if similar light and dark diode parameters are used.

The best approach is then to start simulating the *dark* I-V in which the whole active layer has the same diode parameters. Next, dark parameters are fixed and put into the model for the illuminated experiment. The illuminated part was given the same parameters as for the dark part, except for the photocurrent, see red line in Fig. 9. The result strongly deviates from the experiment. Next the parameters for the illuminated part were adapted to fit the experiment. The result is shown in Fig. 9 by the dashed black line and the corresponding light diode parameters in Table I. Now a nice fit is obtained between the model and experiment.

Table 1. Diode parameters as obtained from fitting the different models to the experimental data

Model	J_0 (A/cm^2)	Rshunt (Ohm cm^2)	n
Lumped series resistance	1×10^{-8}	1.45×10^{4}	1.9
Dark diode parameters from FEM fit	1.54×10^{-10}	5×10^{4}	1.3
Illuminated diode parameters from FEM fit	8×10^{-9}	2×10^{3}	1.6

The parameters for the light and dark diode as given in Table I show substantial differences. The lower shunt resistance of the illuminated diode compared to the dark diode has been reported before[12] where it was suggested that this was due to photodoping of the polymer. But in principle it is not to be expected that n and J_0 would also change upon illumination, as n depends on the morphology of the layer[13] and J_0 depends on the minority charge carrier density and is temperature dependent.[12] Waldauf *et al.* have observed similar trends and introduced a different approach that is based on consistent parameters between dark and illuminated diodes.[12] However, this is a more complicated model in which the photocurrent is voltage dependent, which makes optimization of grid patterns much more difficult. Although our approach is not based on such detailed device physics of the cells, it gives an excellent fit to the light and dark I-V curves for various device lay-outs and can be easily used for optimization of grid patterns. However, it should be checked if this approach also holds at different light intensities.

Fig.10 shows the calculated I-V curves for a cell with the diode parameters from the first fit, i.e. ignoring the dark part, and I-V curves using the light diode parameters as obtained from the fit of the sophisticated model in which different dark and light diodes were taken into account. From this it can be concluded that if the diode parameters from a standard fit of the one-diode model to the experiment are used to optimize polymer solar cells, the efficiency will be underestimated. Since this underestimation amounts to 0.4%-abs (12%-rel), the use of the comprehensive model, with different diode parameters for the dark and the illuminated area, is mandatory.

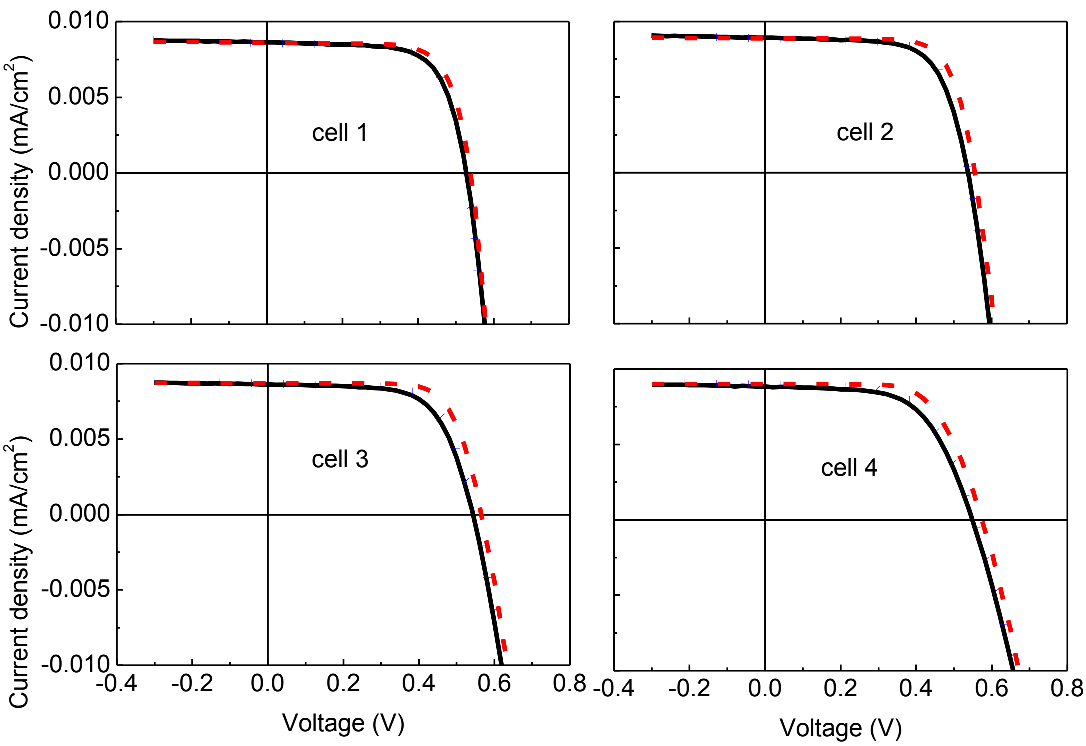

Fig. 9. Experimental I-V curves for all four cells (black,solid), simulated IV curves based on diode parameters obtained from a fit of the dark I-V curve (hence, dark and illuminated part have same diode parameters) (red, dashed) and simulated IV curves with distinct parameters for the dark and illuminated areas (blue, dotted) .

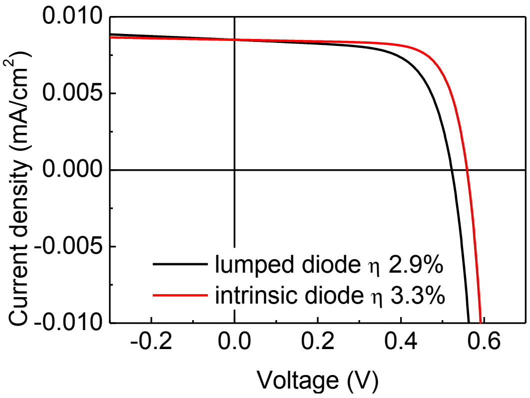

Fig. 10. Simulated curves with (black) diode parameters as obtained from a fit with a lumped series resistance model and (red) with diode parameters as obtained from a fit with a model using different dark and light diode parameters.

5. Conclusions

IV curves have been measured on polymer cells with four different sizes. It was our aim to determine the intrinsic diode parameters of these solar cells, since they are needed for future use in models for solar cell architecture optimization purposes.

Several models were used to simulate IV curves. Per model, four simulated IV curves were simultaneously fitted against their experimental counterparts. Initially, three models were tested: A model with lumped series resistance, a model with distributed series resistance, and a model with distributed series resistance plus an explicit distinction between the illuminated area and the dark area as occurring in the experiment. The fits corresponding to all these three models were not satisfactory. A fourth model was introduced that included the following: Distributed series resistance, distinction between dark and illuminated areas as well as different diode parameters for the dark and illuminated areas. The fits resulting from this comprehensive model were excellent. We have shown that the efficiency derived from the less sophisticated models can lead to an underestimation of 0.4% absolute (12% relative). This clearly shows that the use of the sophisticated model is mandatory.

Acknowledgements

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