The Determination of Effects of Reverse Bias on the Efficiency of Dye Solar Cells with the aid of Spectroscopic and Impedance studies

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Abstract

- The work that is presented here is focused on the results that were obtained during studies of the performance of the DSC under certain reverse bias conditions. When one cell in the series connection in a module is shaded, the current will pass this cell in reverse bias. Although the work is focussed on the chemical stability of the dye, various techniques were employed to determine the physical changes in the cell. This presentation shows how electrochemical and impedance measurements (Nyquist and Bode plots and IV curve data) can compliment spectroscopic measurements (FTIR, Raman, UV-vis) to characterise a dye solar cell.
Structure of the N719 Dye
Electrochemical results
Efficiency vs. Time at Different RB Voltages

-4.5V
-2.5V
-2.0 V
-1.0 V
2V RB and Recovery

![Graph showing efficiency during reverse bias and after reverse bias (recovery).](image-url)
$J_0$ (rate of oxidation or reduction)

\[ J(V) = J \exp \left( \frac{\beta q V}{kT} \right) \]

\[ \text{~for } V < 0 \]

Before reverse bias: $7.2 \times 10^{-11}$ A/cm$^2$

After reverse bias: $8.8 \times 10^{-13}$ A/cm$^2$
IV Curves and Shunt/Series Resistance

<table>
<thead>
<tr>
<th>Condition</th>
<th>$R_{sh}$ (Ω)</th>
<th>$R_s$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before reverse bias</td>
<td>3324</td>
<td>4.3</td>
</tr>
<tr>
<td>Minimum efficiency (turning point)</td>
<td>2517</td>
<td>7.6</td>
</tr>
<tr>
<td>After recovery</td>
<td>3047</td>
<td>5.8</td>
</tr>
</tbody>
</table>
Bode Plots

After 2V

\[ R_{ct} = 100 \, \Omega \]

Before RB

\[ R_{ct} = 340 \, \Omega \]

\[ R_s \]
Nyquist Plots

- Imaginary impedance $-Z''$ (Ω)
- Real impedance $Z'$ (Ω)

Before reverse bias

After reverse bias of 2V
Equivalent Circuit
## Equivalent Circuit and Nyquist Plot

<table>
<thead>
<tr>
<th></th>
<th>Before reverse bias</th>
<th>After reverse bias of 2 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1$</td>
<td>4.73 $\Omega$</td>
<td>4.73 $\Omega$</td>
</tr>
<tr>
<td>$C_1$</td>
<td>1.00 pF</td>
<td>1.00 pF</td>
</tr>
<tr>
<td>$R_2$</td>
<td>12.8 m$\Omega$</td>
<td>15.4 m$\Omega$</td>
</tr>
<tr>
<td>$R_3$</td>
<td>4.73 $\Omega$</td>
<td>4.73 $\Omega$</td>
</tr>
<tr>
<td>$C_2$</td>
<td>22.8 $\mu$F</td>
<td>1.00 pF</td>
</tr>
<tr>
<td>$R_4$</td>
<td>46.8 $\Omega$</td>
<td>146 $\Omega$</td>
</tr>
<tr>
<td>$Q_1$</td>
<td>4.40x10^{-4}</td>
<td>7.98x10^{-4}</td>
</tr>
<tr>
<td>$n_1$</td>
<td>0.833</td>
<td>0.827</td>
</tr>
<tr>
<td>$R_5$</td>
<td>4.73 $\Omega$</td>
<td>4.73 $\Omega$</td>
</tr>
<tr>
<td>$C_3$</td>
<td>10.6 $\mu$F</td>
<td>1.00 pF</td>
</tr>
<tr>
<td>$Q_2$</td>
<td>4.46x10^{-4}</td>
<td>7.97x10^{-4}</td>
</tr>
<tr>
<td>$n_2$</td>
<td>0.834</td>
<td>0.829</td>
</tr>
<tr>
<td>$R_6$</td>
<td>61.3 $\Omega$</td>
<td>208 $\Omega$</td>
</tr>
</tbody>
</table>
Spectroscopic results
UV/Vis

Before RB

540 nm

After

525 nm
Raman

Before RB

After 2V RB and recovery

After 2V RB

Intensity (a.u.)

Raman shift (cm$^{-1}$)

1472, 1540, 1544, 1610

1477, 1544, 1610, 1713

1477, 1611
FTIR

Wavenumber (cm$^{-1}$)

Intensity (a.u.)

- bipyridine $\nu$(C=C) mode at 1542 cm$^{-1}$
- N-C-S 2102
- $\nu$(C=O) shifted to lower frequencies 1715
- COO 1375 and 1635 cm$^{-1}$
- TBA 1470 cm$^{-1}$
- 1237 cm$^{-1}$, ascribed to $\nu$(C-O)
- No indication of a peak at 1354 cm$^{-1}$
FTIR (CN peak at 2100 cm$^{-1}$)
SEM micrographs

Before

After
Conclusions

- Butler Volmer ($J_0$ decreased; reaction rates decreased)
- IV curves (decrease in efficiency and $R_{sh}$)
- Bode Plots (Increase in $R_{ct}$ no change in $R_s$)
- Nyquist plots (Increase in impedance mostly at Pt interface and existence of CPE)
- UV/Vis (Blue shift indicates lower stability)
- Raman (No peak at 1713 – No broken bonds with TiO$_2$; Peak shift at 1540 indicates a change in the bipyridyl ligand)
- FTIR (No indication of free C=O – no broken bonds with TiO$_2$; Decrease in CN peak intensity)
- SEM (No change in morphology)
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