NEW POLYMER ELECTROLYTES OF BIO-BASED POLYURETHANE FOR DYE-SENSITIZED SOLAR CELL APPLICATIONS

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INSTITUTE OF GRADUATE STUDIES
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NEW POLYMER ELECTROLYTES OF BIO-BASED POLYURETHANE FOR
DYE-SENSITIZED SOLAR CELL APPLICATIONS

Field of Study: Applied Science

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ABSTRACT

In this research work, a new bio-based polyurethane (PU) based on castor oil was synthesized as host polymer in electrolytes for application in dye-sensitized solar cell (DSSC). In the first stage of this work, castor oil based polyol was synthesized via transesterification reaction under nitrogen gas atmosphere at room temperature. The polyol possessed acid value of 3.0 mg KOH g\(^{-1}\), hydroxyl value of 190 mg KOH g\(^{-1}\) and molecular weight of 2786 g mol\(^{-1}\), characteristics suitable for producing flexible PU. The polyol was reacted with 4,4’-diphenylmethane diisocyanate at room temperature in appropriate ratios to form flexible PU. The formation of urethane linkage was confirmed using Fourier transform infrared analysis by the disappearance of NCO peak and appearance of amine (secondary), carbonyl and ether group in PU chain. For the preparation of PU polymer electrolytes, the PU was added with sodium iodide (NaI) and lithium iodide (LiI) salts in different weight percentages to form PU-LiI and PU-NaI systems respectively. 3-propyl-1-methylimidazolium iodide (PMII) ionic liquid was added to the highest conducting sample of PU-NaI and PU-LiI systems to enhance the conductivity as well as the efficiency of DSSC. The characteristics of polymer electrolytes were analyzed using Fourier transform infrared spectroscopy, dynamic mechanical analysis, electrochemical impedance spectroscopy, transference number measurement and linear sweep voltammetry. Glass transition temperature of –15.8 °C of PU decreased upon addition of salts. The lowest glass transition temperature of PU-NaI system was –26.2 °C and PU-LiI system was –27.3 °C. The highest conductivity achieved for the systems were 4.28 × 10\(^{-7}\) S cm\(^{-1}\) and 1.41 × 10\(^{-6}\) S cm\(^{-1}\), respectively. The inclusion of PMII ionic liquid to the PU-NaI and PU-LiI enhanced the ionic conductivity of the polymer electrolytes by one order of magnitude and also lowered the \(T_g\) value to \(~ –33.0 \) °C. Ionic liquid is believed to act as plasticizer to soften the polymer backbone.
therefore increase the polymer segmental motion to ease ions migration which in turn increased the ionic conductivity. The conductivity for all PU electrolyte films increased with increase of temperature and follow the Arrhenius behaviour for PU-NaI, PU-LiI and PU-NaI-PMII systems, and Vogel-Tamman-Fulcher behaviour for PU-LiI-PMII. The calculation of activation energy, $E_a$ from the gradient of Arrhenius and Vogel-Tamman-Fulcher plots showed that the trend of conductivity was consistent with the trend of $E_a$, i.e: the higher conducting sample possessed lower activation energy. The addition of ionic liquid to the PU-salt also enhanced electrochemical stability window of the polymer electrolytes. The electrochemical stability windows were $\sim 2.0$ V. DSSCs were fabricated employing PU based polymer electrolytes with configuration of FTO/TiO$_2$-dye/PU electrolytes-I$_2$/Pt/FTO. Photovoltaic parameters such as current density, open circuit voltage, fill factor and efficiency were calculated from photocurrent–voltage measurement. The highest efficiency employing PU-NaI and PU-LiI systems were 0.80% and 0.83%, respectively, whereas for PU-NaI-PMII was 1.06% and PU-LiI-PMII was 1.92%. These results revealed that the new bio polymer electrolytes have potential for application in DSSC.
ABSTRAK

Dalam penyelidikan ini, bio poliuretana (PU) baru berasaskan minyak jarak telah disintesis sebagai polimer perumah dalam elektrolit untuk diaplikasi dalam sel suria terpeka pewarna (DSSC). Pada peringkat awal kajian ini, poliol berasaskan minyak jarak telah disintesis melalui tindak balas transesterifikasi di bawah persekitaran gas nitrogen pada suhu bilik. Poliol yang dihasilkan mempunyai jumlah asid 3.0 mg KOH g⁻¹, jumlah hidroksil 190 mg KOH g⁻¹ dan berat molekul 2786 g mol⁻¹ iaitu ciri-ciri yang sesuai untuk menghasilkan poliuretana yang mudah dibentuk. Poliol telah ditindak balaskan dengan 4,4’-difenilmetilena diisosianat pada suhu bilik dalam nisbah yang sesuai untuk membentuk poliuretana mudah bentuk. Pembentukan jaringan uretana dibuktikan melalui analisis spektroskopi inframerah transformasi Fourier iaitu dengan kehilangan puncak NCO dan kemunculan amina (sekunder), karbonil dan kumpulan eter dalam rantaian PU. Untuk penyediaan elektrolit polimer, PU ditambah dengan garam natrium iodida (NaI) dan litium iodida (LiI) dalam peratusan jisim yang berbeza-beza untuk membentuk sistem sistem PU-NaI dan PU-LiI. 3-propil-1-metilimidazolium iodida (PMII) cecair ionik telah ditambah kepada sampel yang mempunyai kekondusksian paling tinggi dari sistem PU-NaI dan sistem PU-LiI untuk meningkatkan kekondusksian serta kecekapan DSSC. Ciri-ciri elektrolit polimer dianalisis menggunakan spektroskopi inframerah transformasi Fourier, analisis dinamik mekanikal, rintangan elektrokimia spektroskopi, pengukuran nombor pindahan dan voltammetri sapuan linear. Suhu peralihan kaca PU iaitu –15.8 °C menurun apabila garam ditambah kepadanya. Suhu peralihan kaca yang paling rendah pada sistem PU-NaI adalah –26.2 °C dan pada sistem PU-LiI pula adalah –27.3 °C. Kekondusksian tertinggi yang diperolehi dari sistem-sistem ini ialah 4.28 × 10⁻⁷ S cm⁻¹ dan 1.41 × 10⁻⁶ S cm⁻¹. Kemasukan cecair ionik PMII kepada PU-NaI dan PU-LiI telah meningkatkan kekondusksian ionik elektrolit polimer sebanyak
satu magnitud dan juga menurunkan nilai $T_g$ kepada $\sim -33.0 \, ^\circ C$. Cecair ionik dipercayai bertindak sebagai pemplastik untuk melembutkan polimer seterusnya meningkatkan pergerakan segmen polimer untuk memudahkan pergerakan ion-ion, dengan itu meningkatkan kekonduksian ionik. Kekonduksian untuk semua filem elektrolit PU meningkat dengan peningkatan suhu dan mematuhi hukum Arrhenius bagi sistem-sistem PU-NaI, PU-LiI dan PU-NaI-PMII, dan hukum Vogel-Tamman-Fulcher bagi system PU-LiI-PMII. Pengiraan tenaga pengaktifan, $E_a$ dari kecerunan plot Arrhenius dan Vogel-Tamman-Fulcher menunjukkan bahawa nilai kekonduksian konsisten dengan nilai $E_a$, di mana sampel yang berkekonduksian tinggi mempunyai tenaga pengaktifan yang rendah. Penambahan cecair ionik kepada PU-garam juga meningkatkan tetingkap kestabilan elektrokimia elektrolit polimer. Nilai tetingkap kestabilan elektrokimia adalah $\sim 2.0 \, V$. DSSC telah difabrikasi menggunakan elektrolit polimer berasaskan PU dengan konfigurasi FTO/TiO$_2$-pewarna/PU elektrolit-I$_2$/Pt/FTO. Parameter-parameter fotovoltan seperti ketumpatan arus, voltan litar buka, faktor isi dan kecekapan telah dikira dari pengukuran fotoarus-voltan. Kecekapan tertinggi yang diperolehi menggunakan sistem-sistem PU-NaI dan PU-LiI adalah masing-masing 0.80% dan 0.83%, manakala bagi PU-NaI-PMII adalah 1.06% dan PU-LiI-PMII adalah 1.92%. Semua keputusan ini menunjukkan bahawa elektrolit bio polimer baru berasaskan poliuretana dari minyak jarak berpotensi untuk diaplikasi dalam DSSC.
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\( A \) \hspace{1cm} \text{Cross sectional area}
\( C \) \hspace{1cm} \text{Capacitor}
\( E_a \) \hspace{1cm} \text{Activation energy}
\( FF \) \hspace{1cm} \text{Fill factor}
\( I_f \) \hspace{1cm} \text{Final current}
\( I_t \text{ or } I_o \) \hspace{1cm} \text{Initial current}
\( I_{ss} \) \hspace{1cm} \text{Steady state current}
\( I_T \) \hspace{1cm} \text{Total current}
\( J_{sc} \) \hspace{1cm} \text{Short-circuit current density}
\( J-V \) \hspace{1cm} \text{Current density-voltage}
\( k_B \) \hspace{1cm} \text{Boltzmann constant}
\( l \) \hspace{1cm} \text{Thickness}
\( M_w \) \hspace{1cm} \text{Molecular weight}
\( P_{in} \) \hspace{1cm} \text{Incident power}
$P_{\text{max}}$  Maximum power  
$R$  Resistance  
$R_b$  Bulk resistance  
$R_{\text{ct}}$  Charge-transfer resistance  
$R_0$  Bulk resistance before polarization  
$R_{ss}$  Bulk resistance after polarization  
$R_w$  Warburg diffusion impedance  
$T$  Temperature  
$t_{\text{ele}}$  Electronic transference number  
$T_g$  Glass transition temperature  
$t_{\text{ion}}$  Ionic transference number  
$t_{\text{Li}^+}$  Lithium transference number  
$t_{\text{Na}^+}$  Sodium transference number  
$V_{\text{oc}}$  Open-circuit voltage  
wt %  Weight percentage  
$Z$  Impedance  
$Z_R$  Real part of impedance  
$\eta$  Energy conversion efficiency  
$\sigma$  Conductivity  
$\sigma_0$  Pre-exponential factor of conductivity
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>AlCl₄⁻</td>
<td>Tetrachloroaluminate</td>
</tr>
<tr>
<td>AM</td>
<td>Air Mass</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated Total Reflectance</td>
</tr>
<tr>
<td>BD</td>
<td>1,4-Butanediol</td>
</tr>
<tr>
<td>BMII</td>
<td>1-butyl-3-methylimidazolium iodide</td>
</tr>
<tr>
<td>Br⁻/Br₂</td>
<td>Bromine/bromide</td>
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<tr>
<td>CB</td>
<td>Conduction band</td>
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<td>Cobalt telluride</td>
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</tr>
<tr>
<td>CPE</td>
<td>Constant phase element</td>
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<tr>
<td>CZTS</td>
<td>Copper-zinc tin sulfide</td>
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<tr>
<td>DBP</td>
<td>Dibutyl phthalate</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DEC</td>
<td>Diethyl carbonate</td>
</tr>
<tr>
<td>DEG</td>
<td>Diethylene glycol</td>
</tr>
<tr>
<td>DEP</td>
<td>Diethyl phthalate</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic Mechanical Analysis</td>
</tr>
<tr>
<td>DMII</td>
<td>1,3-dimethylimidazolium iodide</td>
</tr>
<tr>
<td>DMPII</td>
<td>1,2-dimethyl-3-propylimidazolium iodide</td>
</tr>
<tr>
<td>DMPP</td>
<td>2,2-dimethoxy-2-phenylacetophenone</td>
</tr>
<tr>
<td>DSSC</td>
<td>Dye-sensitized solar cells</td>
</tr>
<tr>
<td>EC</td>
<td>Ethylene Carbonate</td>
</tr>
<tr>
<td>EGMEM</td>
<td>Ethylene glycol methyl ether methacrylate</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>EMIBF₄</td>
<td>1-ethyl-3-methylimidazolium tetrafluoroborate</td>
</tr>
<tr>
<td>EMII</td>
<td>1-ethyl-3-methylimidazolium iodide</td>
</tr>
<tr>
<td>EMImTFSI</td>
<td>1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide</td>
</tr>
<tr>
<td>EMISCN</td>
<td>1-ethyl-3-methylimidazolium thiocyanate</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine-doped tin oxide, SnO₂:F</td>
</tr>
<tr>
<td>GMA</td>
<td>Glycidyl methacrylate</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel permeation chromatography</td>
</tr>
<tr>
<td>GPE</td>
<td>Gel polymer electrolyte</td>
</tr>
<tr>
<td>H₁₂MDI</td>
<td>4,4′-methylenebis(cyclohexyl isocyanate)</td>
</tr>
<tr>
<td>HBPU</td>
<td>Hyperbranched polyurethane</td>
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<tr>
<td>Hex₄NI</td>
<td>Tetrahexylammonium iodide</td>
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<tr>
<td>HMII</td>
<td>1-hexyl-3-methylimidazolium iodide</td>
</tr>
<tr>
<td>Symbol</td>
<td>Name</td>
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<tr>
<td>--------</td>
<td>-------------------------------------------</td>
</tr>
<tr>
<td>I/3^-</td>
<td>Iodide-triiodide</td>
</tr>
<tr>
<td>I₂</td>
<td>Iodine</td>
</tr>
<tr>
<td>IL</td>
<td>Ionic liquid</td>
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<tr>
<td>IPDI</td>
<td>Isophorone disocyanate</td>
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<tr>
<td>KI</td>
<td>Potassium iodide</td>
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<tr>
<td>KOH</td>
<td>Potassium hydroxide</td>
</tr>
<tr>
<td>Li₃N</td>
<td>Lithium nitride</td>
</tr>
<tr>
<td>LiAl₂O₃</td>
<td>Lithium aluminum oxide</td>
</tr>
<tr>
<td>LiAsF₆</td>
<td>Lithium hexafluoroarsenate (V)</td>
</tr>
<tr>
<td>LiBF₄</td>
<td>Lithium tetrafluoroborate</td>
</tr>
<tr>
<td>LiBr</td>
<td>Lithium bromide</td>
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<tr>
<td>LiCF₃SO₃</td>
<td>Lithium trifluoromethane sulfonate</td>
</tr>
<tr>
<td>LiClO₄</td>
<td>Lithium perchlorate</td>
</tr>
<tr>
<td>LiI</td>
<td>Lithium iodide</td>
</tr>
<tr>
<td>LiN(SO₂CF₃)₂</td>
<td>Lithium bis(tri-fluoromethanesulfonyl)imide</td>
</tr>
<tr>
<td>LiTf</td>
<td>Lithium triflate</td>
</tr>
<tr>
<td>LiTFSI</td>
<td>Lithium bis(tri-fluoromethanesulfonyl)imide</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear sweep voltammetry</td>
</tr>
<tr>
<td>MDI</td>
<td>4,4’-diphenylmethane diisocyanate</td>
</tr>
<tr>
<td>MgI₂</td>
<td>Magnesium iodide</td>
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<tr>
<td>MMT</td>
<td>Montmorillonite</td>
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<tr>
<td>N₃</td>
<td>cis-Bis(isothiocyanato) bis(2,2’-bipyridyl-4,4’-dicarboxylato ruthenium(II))</td>
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<tr>
<td>N-719</td>
<td>di-tetradecylammonium cis-bis(isothiocyanato) bis(2,2’-bipyridyl-4,4’-dicarboxylato) ruthenium (II) dye</td>
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<tr>
<td>NaI</td>
<td>Sodium iodide</td>
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<tr>
<td>NaTf</td>
<td>Sodium trifluoromethanesulfonate</td>
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<tr>
<td>Nb₂O₅</td>
<td>Niobium pentoxide</td>
</tr>
<tr>
<td>Acronym</td>
<td>Full Form</td>
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<td>-----------</td>
<td>-----------------------------------------------------</td>
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<tr>
<td>NCO</td>
<td>Isocyanate</td>
</tr>
<tr>
<td>NiTe$_2$</td>
<td>Nickel telluride</td>
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<tr>
<td>NMBI</td>
<td>N-methylbenzimidazole</td>
</tr>
<tr>
<td>NR</td>
<td>Natural rubber</td>
</tr>
<tr>
<td>OH</td>
<td>Hydroxyl</td>
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<tr>
<td>P(EO-EPI)</td>
<td>Poly(ethylene oxide-co-epichlorohydrin)</td>
</tr>
<tr>
<td>P(MMA-co-EMA)</td>
<td>Poly(methyl methacrylate-co-ethyl methacrylate)</td>
</tr>
<tr>
<td>PA</td>
<td>Phthalic anhydride</td>
</tr>
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<td>PAN</td>
<td>Polyacrylonitrile</td>
</tr>
<tr>
<td>PC</td>
<td>Propylene carbonate</td>
</tr>
<tr>
<td>PDMS-g PEO</td>
<td>Poly[dimethylsiloxane-g-poly(ethylene oxide)]</td>
</tr>
<tr>
<td>PEDOT</td>
<td>Poly(3,4-ethylenedioxythiophene)</td>
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<tr>
<td>PEDOT:PSS</td>
<td>Poly(3,4-ethylenedioxythiophene):poly(styrene</td>
</tr>
<tr>
<td></td>
<td>sulfonate)</td>
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<tr>
<td>PEG</td>
<td>Poly(ethylene glycol)</td>
</tr>
<tr>
<td>PEM</td>
<td>Poly(methoxy polyethylene glycol monomethacrylates)</td>
</tr>
<tr>
<td>PEMA</td>
<td>Poly(ethyl methacrylate)</td>
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<tr>
<td>PEMPS</td>
<td>Polyether modified polysiloxane</td>
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<tr>
<td>PEO</td>
<td>Poly(ethylene oxide)</td>
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<td>PEs</td>
<td>Polymer electrolytes</td>
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<tr>
<td>PET</td>
<td>Poly(ethylene terphthalate)</td>
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<td>PHEA</td>
<td>Poly(hydroxyethylacrylate)</td>
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<tr>
<td>PMII</td>
<td>3-propyl-1-methylimidazolium iodide</td>
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<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
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<tr>
<td>PPG</td>
<td>Poly(propylene) glycol</td>
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<tr>
<td>Pr$_4$NI</td>
<td>Tetrapropylammonium iodide</td>
</tr>
<tr>
<td>Pt</td>
<td>Platinum</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
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<tr>
<td>PTMG</td>
<td>Poly(tetramethylene glycol)</td>
</tr>
<tr>
<td>PU</td>
<td>Polyurethane</td>
</tr>
<tr>
<td>PVA or PVAc</td>
<td>Polyvinyl acetate</td>
</tr>
<tr>
<td>PVC</td>
<td>Poly(vinyl chloride)</td>
</tr>
<tr>
<td>PVDF</td>
<td>Poly(vinylidene fluoride)</td>
</tr>
<tr>
<td>PVDF-HFP</td>
<td>Poly(vinylidene fluoride-co-hexafluoropropylene)</td>
</tr>
<tr>
<td>PVP</td>
<td>Poly(vinyl pyrolidone)</td>
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<tr>
<td>PYRA_{120}TFSI</td>
<td>N-ethyl(methylether)-N-methylpyrrolidinium trifluoromethanesulfonimate</td>
</tr>
<tr>
<td>RE</td>
<td>Reference electrode</td>
</tr>
<tr>
<td>RS</td>
<td>Rice starch</td>
</tr>
<tr>
<td>(SeCN)$_2$</td>
<td>Selenocyanogen</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Silicon oxide</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>Tin oxide</td>
</tr>
<tr>
<td>SPE</td>
<td>Solid polymer electrolyte</td>
</tr>
<tr>
<td>SS</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>TBAI</td>
<td>Tetrabutylammonium iodide</td>
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<tr>
<td>TBP</td>
<td>4-tert-butylpyridine</td>
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<tr>
<td>TCO</td>
<td>Transparent conducting oxide</td>
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<td>TDI</td>
<td>Toluene diisocyanate</td>
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<td>TGA</td>
<td>Thermogravimetric analysis</td>
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<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
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<td>TiO$_2$</td>
<td>Titanium oxide</td>
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<td>TPU</td>
<td>Thermoplastic polyurethane</td>
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<tr>
<td>VTF</td>
<td>Vogel-Tamman-Fulcher</td>
</tr>
<tr>
<td>WE</td>
<td>Working electrode</td>
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<tr>
<td>ZnO</td>
<td>Zinc oxide</td>
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