

Pulse power characteristics of poly(3-methylthiophene) cathodes in $\text{Li}(\text{SO}_2)_3\text{AlCl}_4$ electrolyte

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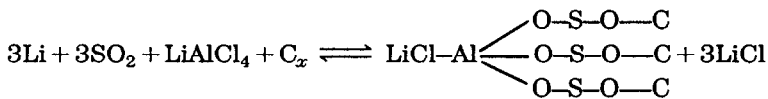
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Abstract

Thin, electrically conducting poly(3-methylthiophene) (PMT) films were formed electrochemically and used as cathodes in rechargeable lithium/sulfur dioxide cells. The pulse power capabilities of $1.4 \mu\text{m}$ thick PMT films were studied in $\text{Li}(\text{SO}_2)_3\text{AlCl}_4$ electrolyte. Current densities of 56 mA cm^{-2} (800 W cm^{-3}) were measured 0.5 s after applying a 1.46 V potential step from open circuit to 2.0 V. Multiple four second current pulses of 25 mA cm^{-2} (approximately 500 W cm^{-3}) with one second rest periods between pulses were reproducible over many cycles.

Introduction

Rechargeable lithium/ SO_2 cells containing $\text{Li}(\text{SO}_2)_x\text{AlCl}_4$ electrolyte (where $x > 1$) have been studied with various porous carbon cathodes or electrically conducting polymer cathodes [1–3]. Based on cell performance and analytical data, Dey *et al.* [1] postulated the cell reaction to involve the formation of a complex between the carbon cathode and SO_2 .



Research has generally focused on optimizing cathode capacity, cell rechargeability and safety. There is also interest in the pulse power characteristics of this system for reserve cells and for pulse applications. Because pulse power is derived predominantly at the electrode surface (rather than the interior bulk), thin polymer electrodes are both efficient and well suited for bipolar construction employing many electrodes. Poly(3-methylthiophene) cathodes have been cycled at low rates in lab cells containing $\text{Li}(\text{SO}_2)_3\text{AlCl}_4$ electrolyte (conductivity $10^{-1} \text{ S cm}^{-1}$) without exceeding 3.8 V on charge [3]. Charging at potentials below 4.0 V minimizes chlorine formation, thereby reducing corrosion of lithium. An attractive feature of PMT is that, depending on the method of preparation and dopant anion, it has an electrical conductivity in the range of 10–2000 S cm^{-1} [4–7]. The high conductivities of $\text{Li}(\text{SO}_2)_3\text{AlCl}_4$

electrolyte and PMT cathodes should minimize cell impedance losses, which are of particular concern for pulse systems.

In this study, thin (1.4 μm thick) polymer films were electrochemically formed from the polymerization of 3-methylthiophene and pulse discharged in $\text{Li}(\text{SO}_2)_3\text{AlCl}_4$ electrolyte. We report the results of potential step experiments where delivered currents were measured and power densities calculated for up to five seconds following the applied pulses. Current pulses were also applied to determine the ability of PMT to accommodate high constant currents over pulse periods of several seconds.

Experimental

Polymerization of PMT was carried out in a 125 ml European style flask (Ace Glass) using a 1 cm^2 platinum flag counter electrode, a SSCE reference electrode, and a platinum or glassy carbon rod working electrode. Glassy carbon and platinum rods (0.071 cm^2 cross section) were polished to a mirror finish with a 0.1 μm alumina/water paste. The rod was sheathed in heat shrinkable Teflon so as to expose only the cross-sectional area at the end of the rod. The cell was flooded with electrolyte containing 0.1 M 3-methylthiophene monomer (Sigma Chemical, 99+%) and 0.1 M tetrabutylammonium tetrafluoroborate (Alpha), in acetonitrile (Fisher) that had been redistilled while bubbling dry argon. Ultra high purity dry argon was also bubbled through the electrolyte to remove oxygen.

PMT polymerization occurred when the potential (working versus reference) was ≥ 1.5 V. Passing 0.25 C cm^{-2} at 7 mA cm^{-2} constant current produced a 0.41 μm thick film (as measured by SEM) which strongly adhered to the substrate. Thicker films, containing 1.25 C cm^{-2} , could not be prepared at 7 mA cm^{-2} since the potential slowly fell below 1.5 V during polymerization. Higher currents (10 mA cm^{-2}) produced a mossy, dendritic, non-adherent polymer film. However, 1.4 μm thick adherent films were fabricated at 10 mA cm^{-2} by a pulse deposition process, where 0.25 C cm^{-2} was passed in five cycles with five minute rest periods (at open circuit) between cycles. The PMT-coated rod was then rinsed in acetonitrile and dried under vacuum at 50 $^\circ\text{C}$. Based on the number of coulombs passed, to a first approximation (assuming 100% plating efficiency), a maximum of 4.52×10^{-5} g of 3-methylthiophene was deposited on the substrate.

A miniature porous carbon electrode, similar in size to the PMT electrode, was constructed with Shawinigan acetylene black without the use of Teflon binder. It was prepared as described elsewhere [8] by coating the exposed cross-sectional end (0.098 cm^2) of a Teflon-sheathed glassy carbon rod with conducting silver epoxy (AESAR Mattheylec A-500). Prior to curing, the epoxy-covered end was pressed into a tube containing the Shawinigan carbon black and then removed. After drying overnight under vacuum at 50 $^\circ\text{C}$, excess carbon was removed by gentle agitation in a water-acetone solution and dried again. The rod was lightly rubbed across a piece of paper to

smooth out the contour. By this procedure we were able to prepare porous carbon electrodes between 20 and 50 μm thick.

$\text{Li}(\text{SO}_2)_3\text{AlCl}_4$ electrolyte was prepared with anhydrous LiAlCl_4 (Anderson Physics) and excess dry liquid SO_2 (Matheson) by combining them in an evacuated Teflon cell (able to withstand pressure). After dissolution of the salt, excess SO_2 was slowly bled off through a bubbler containing halocarbon oil. The resultant electrolyte had between 3 and 3.5 SO_2 molecules per LiAlCl_4 molecule as measured by weight. Anhydrous LiCl was added to scavenge any excess AlCl_3 and ensure a neutral electrolyte.

Potential pulse experiments were performed with a PAR model 173 potentiostat/galvanostat and a model 276 plug-in interface, used in conjunction with PAR model 175 universal programmer. The potential was stepped from open circuit to either 2.6 or 2.0 V (versus Li). Current and potential were followed on a Nicolet 4094C digital oscilloscope, with data points taken at either 2 or 100 μs intervals. The experimental cell for the pulse experiments was a 125 ml European flask flooded with 20 ml of $\text{Li}(\text{SO}_2)_3\text{AlCl}_4$ electrolyte, containing a large lithium counter electrode and lithium reference. All experiments were performed at 25 $^\circ\text{C}$ with 1.4 μm thick PMT cathodes.

Polymerization of PMT and constant current pulse experiments were performed galvanostatically, controlled with a Hewlett Packard HP-86 computer. Upon polymerization in $\text{Bu}_4\text{NBF}_4\text{-CH}_3\text{CN}$ electrolyte, PMT is doped with BF_4^- anions. We previously reported [3] that after constant current discharge and recharge of PMT (containing BF_4^-) in $\text{Li}(\text{SO}_2)_3\text{AlCl}_4$ electrolyte, subsequent discharge capacity of PMT (now doped with AlCl_4^- anions) improved. In fact, others have commonly observed better performance after a 'break-in' period. Kawai *et al.* [9] observed an increase in cycling efficiency with cycle number for various poly(3-alkylthiophenes). They attributed this to two effects; an accumulation of dopant ions trapped in the polymer, and secondly, a structural change of the polymer matrix which allows dopant ions to migrate more easily within the polymer. Pern and Frank [10] also had evidence of these two effects based on data obtained for PMT. Likewise, we presume that the polymer lattice of AlCl_4^- -doped PMT is expanded, facilitating diffusion of ions and creating more surface area for contact with the electrolyte. This would explain the increase in discharge capacities seen during the first few cycles. As a result of this observation, all pulse experiments were performed with AlCl_4^- -doped PMT. The method of treatment was to first undope BF_4^- from the polymer in $\text{Li}(\text{SO}_2)_3\text{AlCl}_4$ electrolyte by holding the potential at 3.0 V (versus lithium) and then doping PMT with AlCl_4^- by charging at a constant potential of 3.7–3.8 V. These potentials were based on cyclic voltammetric studies where a large reduction peak at 2.74 V and an oxidation peak at 3.74 V were observed. We assumed that minimal electrolyte reduction would occur while undoping the polymer at 3.0 V. After doping with AlCl_4^- (at 3.8 V) and standing overnight, the cell potential equilibrated at 3.4 V.

We attempted to alleviate the undoping and doping steps by polymerizing PMT in the presence of tetrabutylammonium tetrachloroaluminate or lithium

tetrachloroaluminate salts, hoping to prepare polymer that already contained the AlCl_4^- dopant. Although PMT was formed, films poorly adhered to the substrate and were unsuitable as electrodes.

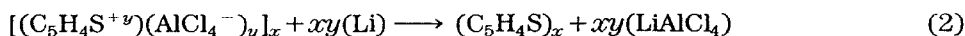
Results and discussion

SEM photographs showed a compact layer of polymer attached to the substrate, with irregularly shaped nodules deposited on the surface. A one point BET gas adsorption surface area analysis (performed by Micromeritics, Norcross, GA) indicated that PMT polymerized at 10 mA cm^{-2} (as was the $1.4 \mu\text{m}$ thick film) had an area of $4.13 \text{ m}^2 \text{ g}^{-1}$. Based on the cross-sectional area and thickness, the $1.4 \mu\text{m}$ thick PMT had a volume of $9.95 \times 10^{-6} \text{ cm}^3$.

Discharge of PMT in $\text{Li}(\text{SO}_2)_3\text{AlCl}_4$ involves two processes, reduction (undoping) of the polymer and reduction of the electrolyte. The theoretical energy derived from polymer undoping alone can be calculated by

$$\frac{\text{A h}}{\text{kg}} = \frac{(96480 \text{ C/F})(1000 \text{ g/kg})}{(\text{g/F})(3600 \text{ s/h})} = \frac{26800}{(\text{g/F})} \quad (1)$$

Writing the overall discharge reaction and solving for g/F by inserting the formula weights for the electroactive species we have:



$$\text{g/F} = \frac{x(\text{C}_5\text{H}_4\text{S}) + xy(\text{LiAlCl}_4)}{xy} \quad (3)$$

$$\text{g/F} = \frac{x(96.15) + xy(175.7)}{xy} \quad (4)$$

$$\text{g/F} = \frac{96.15}{y} + 175.7 \quad (5)$$

where y represents the percent doping.

Based on an optimistic doping level of 50% ($y=0.5$), we calculate a theoretical energy of 72.8 A h kg^{-1} for fully undoping PMT. Using an operating load voltage of 3.1 V reported for constant current discharge in $\text{Li}(\text{SO}_2)_3\text{AlCl}_4$ electrolyte [3], we arrive at $225.7 \text{ W h kg}^{-1}$ (assuming we could achieve 100% undoping at this potential). A more realistic dopant level of 35% yields theoretical values of 59.5 A h kg^{-1} and $184.5 \text{ W h kg}^{-1}$. In fact, a dopant level of less than 50% would be preferred based on the work of Ofer *et al.* [11], who have determined that there is a potential window of high conductivity. As neutral (insulating) polymer is oxidized and dopant level is increased, a maximum in conductivity is attained beyond which conductivity decreases with further oxidation. They found that maximum conductivity for PMT occurred at ≈ 0.3 electrons per repeat unit, and beyond ≈ 0.5 electrons per repeat unit thiophenes tended to decompose. Other evidence arguing for

doping levels of about 30% was shown in studies with poly(3-octylthiophene) by Kawai *et al.* [9]. They determined a coulombic efficiency of only 47% at a maximum doping level of 48.6%, whereas at a 33% doping level efficiency was 94%.

Pulse experiments were conducted by stepping the potential from open circuit to ≤ 2.6 V, which is more cathodic than the main reduction peak observed for $\text{Li}(\text{SO}_2)_3\text{AlCl}_4$ using cyclic voltammetry. This ensured the simultaneous reduction of both the electrolyte and PMT. Based on the maximum mass (4.52×10^{-8} kg) of PMT polymerized, theoretical capacity due to complete polymer undoping from the 35% level would be 2.69×10^{-6} A h. However, this would not be possible since PMT would become electrically insulating before all of this charge could be removed. Constant current discharge at 1.0 mA cm^{-2} showed that PMT delivered a capacity 5.3×10^{-5} A h, which is 20 times greater than expected if capacity were due to undoping alone. Based on this, we assume that the majority of the pulse discharge capacity was likewise derived from reduction of the SO_2 electrolyte.

Figure 1 compares current density as a function of the inverse square root of time during the first 13 ms following a potential step from open circuit for $1.4 \mu\text{m}$ thick PMT and $25 \mu\text{m}$ thick porous carbon electrodes. Stepping the potential to 2.0 V, PMT delivered more than twice the current ($\approx 1130 \text{ mA cm}^{-2}$) as did porous carbon ($\approx 480 \text{ mA cm}^{-2}$), achieving over 2 W cm^{-2} for nearly $100 \mu\text{s}$. When PMT was pulsed only to 2.6 V, current density remained about 50% higher than that obtained with porous carbon for up to $400 \mu\text{s}$. The superior pulse power of PMT compared to porous carbon is not a result of polymer surface area ($4.13 \text{ m}^2 \text{ g}^{-1}$) since Shawinigan black has a greater surface area ($60 \text{ m}^2 \text{ g}^{-1}$).

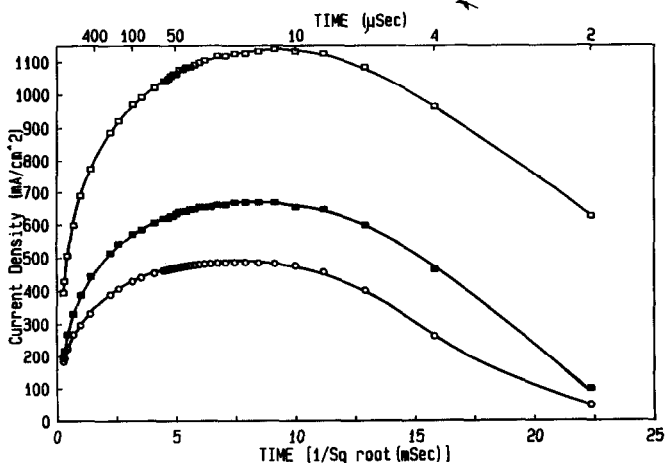


Fig. 1. Current density as a function of the inverse square root of time (up to 13 ms) following a potential step from open circuit in a cell containing a Li anode and $\text{Li}(\text{SO}_2)_3\text{AlCl}_4$ electrolyte. Cathodes were $1.4 \mu\text{m}$ thick PMT stepped to 2.0 V (\square) and 2.6 V (\blacksquare), and $25 \mu\text{m}$ thick Shawinigan carbon cathode (\circ) stepped to 2.0 V.

Bare platinum or glassy carbon electrodes (not shown) delivered approximately 800 mA cm^{-2} for up to $10 \mu\text{s}$ when stepped to 2.0 V , but currents rapidly fell thereafter. The first few μs after pulsing reflected the contribution due to double layer capacitance, and the period following this indicated the maximum current that could be contributed from electrolyte reduction on the substrate. Thus, any current that might rise from reduction processes on the substrate would be small and short-lived.

Power (and current) density for up to 0.5 s following a potential step from OCV to 2.0 V is shown in Fig. 2. Almost no current arises from the glassy carbon (or platinum) substrate beyond 10 ms , indicating again that any current contributions from the substrate were negligible. Although $25 \mu\text{m}$ thick porous electrodes provided 20 mA cm^{-2} out to 0.5 s , PMT delivered nearly three times the current (56 mA cm^{-2}) and a power density of 800 W cm^{-3} at 0.5 s . In a smaller potential step, to 2.6 V (not shown), PMT delivered 42 mA cm^{-2} (780 W cm^{-3}) after 0.5 s . Total charge delivered during potential steps to 2.6 and 2.0 V is given for several time periods in Figs. 3 and 4. PMT was able to deliver more than twice the charge of porous carbon up to 500 ms . Although the total charge passed by PMT was higher for the 2.0 V pulse, power density after 0.5 s was similar for pulses to 2.0 and 2.6 V (800 and 780 W cm^{-3} , respectively). This indicates that by 0.5 s the discharge process is largely diffusion limited, and larger pulses will not result in significantly more power. So for a relatively long (0.5 s) pulse period, a shallow pulse to 2.6 V is sufficient, and also allows PMT to be more easily recharged than if it were discharged to lower potentials.

In Table 1, current and power density (potential step to 2.6 V) are shown for up to 5 s . Very high current densities ($> 100 \text{ mA cm}^{-2}$) occurred during the first second, however, currents fell to 26 mA cm^{-2} ($\approx 0.07 \text{ W}$

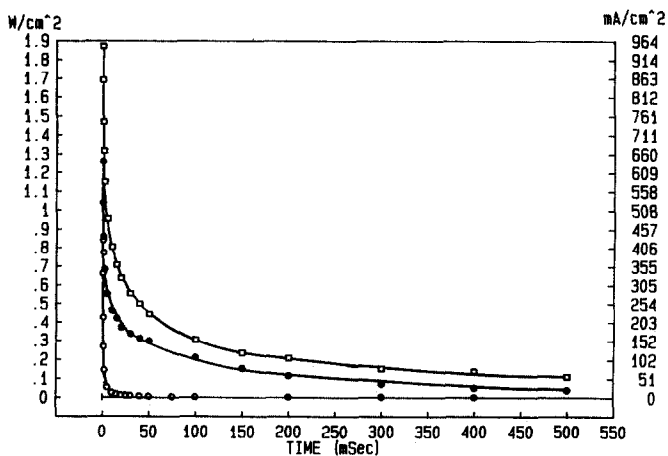


Fig. 2. Power and current density as a function of time for up to 0.5 s after a potential step from open circuit to 2.0 V . Cathodes were $1.4 \mu\text{m}$ thick PMT (\square), $25 \mu\text{m}$ thick Shawinigan carbon (\bullet), and glassy carbon (\circ).

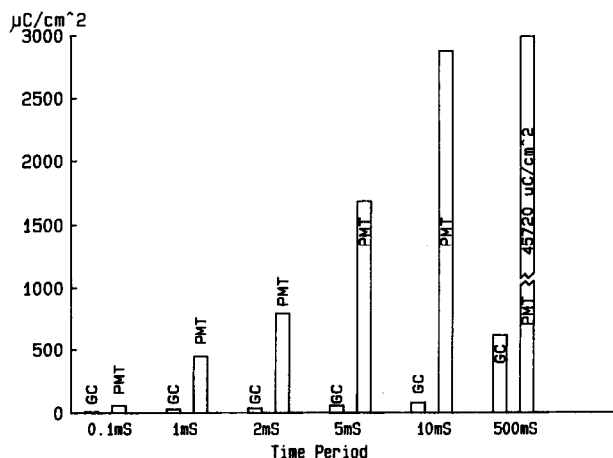


Fig. 3. Total charge delivered over various time periods for glassy carbon (GC) and 1.4 μm thick PMT cathodes in $\text{Li}(\text{SO}_2)_3\text{AlCl}_4$ electrolyte, stepped from open circuit to 2.6 V.

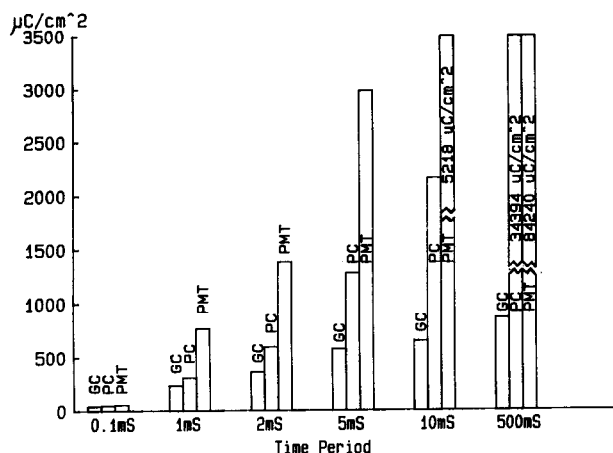


Fig. 4. Total charge delivered over various time periods for glassy carbon (GC), 25 μm thick Shawinigan porous carbon (PC) and 1.4 μm thick PMT cathodes in $\text{Li}(\text{SO}_2)_3\text{AlCl}_4$ electrolyte, stepped from open circuit to 2.0 V.

cm^{-2} , 489 W cm^{-3}) after 5 s. Mass transport limits the ability to sustain high power for longer periods. These short-lived high power pulses might be suitable for pulse applications with cells configured in a bipolar arrangement consisting of many electrodes.

Thicker PMT electrodes containing twice the amount of material used to form the 1.4 μm thick film were also pulsed, but measured currents were the same as for the 1.4 μm thick PMT. Further, constant current discharge capacity of these thicker films showed only marginal improvement, so it was concluded that PMT films thicker than 1.4 μm offer no advantage.

TABLE 1

Comparison of current density and power density for 1.4 μm thick PMT in $\text{Li}/\text{Li}(\text{SO}_2)_3\text{AlCl}_4/\text{PMT}$ cell stepped from OCV to 2.6 V

Time (s)	Current density (A cm^{-2})	Power density (W cm^{-2})
0.001	0.723	1.880
0.01	0.479	1.245
0.1	0.273	0.710
1.0	0.126	0.328
2.0	0.063	0.164
3.0	0.041	0.107
4.0	0.033	0.086
5.0	0.026	0.068

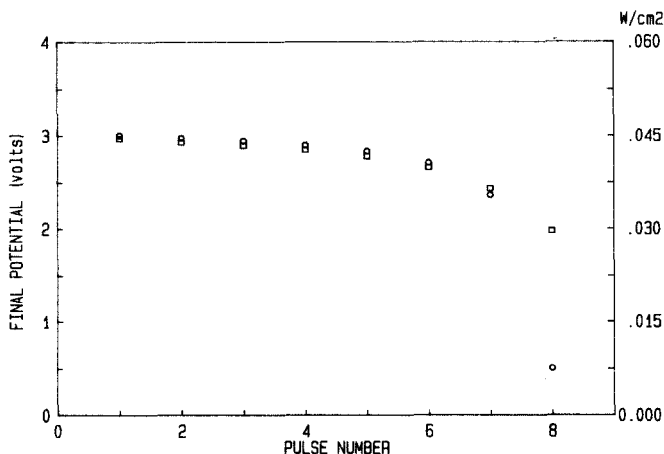


Fig. 5. Final potential of $\text{Li}/\text{Li}(\text{SO}_2)_3\text{AlCl}_4/1.4 \mu\text{m}$ PMT cell after each 4 s, 15 mA cm^{-2} pulse with 1 s open circuit rest periods. Recharge was at 0.2 mA cm^{-2} to a 3.8 V cutoff. First (\square) and 21st (\circ) pulse sets.

PMT was also evaluated for intermittent constant current pulse power capability. A constant current load was applied for 4 s, and cell potential measured at the end of this period. Following a one second rest at open circuit, the cell was pulsed again. This procedure was repeated until cell potential fell below 2.0 V. The cell was then recharged at 0.2 mA cm^{-2} to a 3.8 V cutoff, after which the next cycle was begun. Figure 5 shows the final potential and power density when PMT was discharged at 15 mA cm^{-2} . PMT was pulse discharged for twenty-one cycles (arbitrary number of cycles), with each cycle providing eight pulses. Except for the last pulse in each set, final potentials were remarkably similar even after 21 cycles. During the first six pulses, the final potential ranged between 3.0 V on the first pulse and 2.7 V on the sixth pulse, corresponding to power densities of 0.045

and 0.040 W cm^{-2} (321 and 289 W cm^{-3} , respectively). At a 25 mA cm^{-2} rate, four to five pulses were obtained for 35 cycles. Only the first three pulses were reproducible, with final potentials between 2.9 and 2.6 V, and power densities of 518 to 464 W cm^{-3} , respectively. At 50 mA cm^{-2} , PMT was able to deliver only one or two pulses to cutoff. These experiments demonstrated the ability of PMT to deliver several pulses over a short time period, and then to be reproducibly repeated for several cycles.

Conclusions

PMT was electrochemically polymerized as a $1.4 \mu\text{m}$ film directly onto a supporting substrate. PMT cathodes used in rechargeable Li/SO₂ cells containing Li(SO₂)₃AlCl₄ electrolyte delivered sub-second pulse power in excess of 100 mA cm^{-2} , and over 1 A cm^{-2} for nearly $100 \mu\text{s}$. Potential step pulses from open circuit to 2.6 V delivered power densities of 42 mA cm^{-2} (780 W cm^{-3}) after 0.5 s, and 26 mA cm^{-2} (489 W cm^{-3}) after 5 s. Multiple four second constant current pulses at 25 mA cm^{-2} yielded a power density of approximately 500 W cm^{-3} . PMT could be recharged and reproducibly pulse discharged for many cycles.

Acknowledgement

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