

**HIGH PERFORMANCE ULTRACAPACITORS WITH GRAPHENE-
BASED COMPOSITE ELECTRODES**

FILE NO. YSS/2015/000765

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Assam 784028

PROJECT COMPLETION REPORT

1a. Title of the project: **High performance ultracapacitors with graphene-based composite electrodes**

1b. File No.: **FILE NO. YSS/2015/000765**

2. Principal Investigator: **Shyamal Kumar Das**

3. Implementing Institution: **Tezpur University, Assam-784028**

4. Date of commencement: : 24-11-2015

5. Planned date of completion: : 24-11-2018

6. Actual date of completion: : 24-11-2018

7. Objectives as stated in the project proposal:

The various proposed objectives of the project are as follows:

i. Synthesis of composites of porous graphene-nanosized metal oxides-amorphous carbon by simple hydrothermal routes.

ii. Determination of structure property correlation of the synthesized materials using analytical and structural tools.

iii. Electrochemical evaluation of the synthesized composites. The evaluation comprises of galvanostatic cycling and cyclic voltammetry testing.

iv. Optimization of the ultracapacitor performance from ex-situ structural and electrochemical analysis.

8. Deviation made from original objectives if any, while implementing the project and reasons thereof:

There is subtle deviation while writing the articles. Although all the articles were written mentioning the key word “aqueous Al-ion battery”, essentially it also represents aqueous Al-ion ultracapacitors. While investigating the electrode materials, we introduced a new approach of using aqueous Al electrolytes rather than conventional aqueous electrolytes such as KOH, HCl, H₂SO₄ etc. That is why we introduced the term aqueous Al-ion battery in all our articles. It would also be correct if the term aqueous Al-ion capacitor is used. All the scientific contents and experiments are same as proposed in the proposal.

9. Experimental work giving full details of experimental set up, methods adopted, data collected supported by necessary table, charts, diagrams & photographs:

As proposed, we undertook hydrothermal synthesis methodology to process various electrode materials such as graphene-MoO₃, graphene-WO₃, graphene-TiO₂, graphene-MnO₂ and graphene-Fe₂O₃. These electrode materials were characterized by several techniques such as powder x-ray diffraction, scanning electron microscopy and transmission electron microscopy, Raman spectroscopy etc. Surface area/porosity and carbon content of the

composites were analysed using nitrogen adsorption-desorption isotherms and thermogravimetric analysis respectively. Detailed electrochemical investigation on the electrode materials were performed using Biologic SP300 electrochemical work station in conventional three electrode and two electrode systems.

Some of the important data obtained during the execution of the project are shown below.

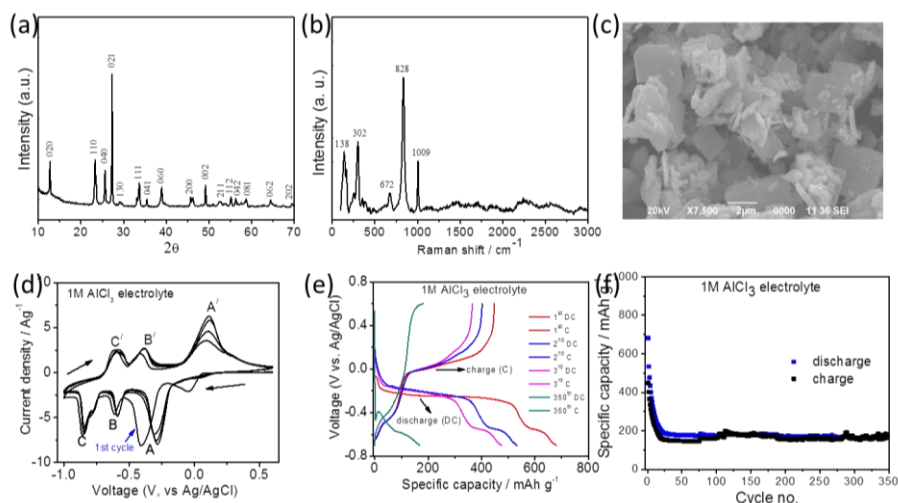


Figure 1: (a) XRD pattern, (b) Raman spectrum and (c) SEM image of MoO_3 . (d) CV profiles of MoO_3 in 1 M AlCl_3 , (e) Galvanostatic discharge/charge curves of MoO_3 at current of 2.5 Ag^{-1} . (f) Variation of charge/discharge capacities with cycle number.

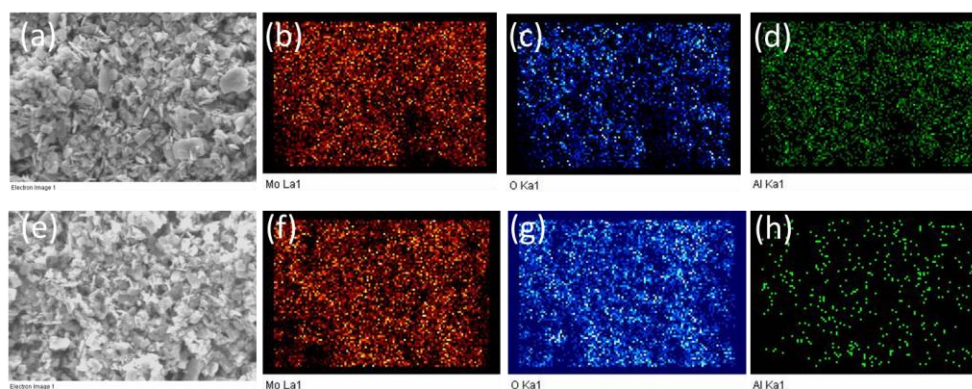


Figure 2. (a) SEM image of scanned area for elemental mapping of 1st discharge state MoO_3 electrode. Elemental mapping images of (b) Mo, (c) O and (d) Al of the 1st discharge state electrode. (e) SEM image of scanned area for elemental mapping of 1st charge state MoO_3 electrode. Elemental mapping images of (f) Mo, (g) O and (h) Al of the 1st charge state electrode.

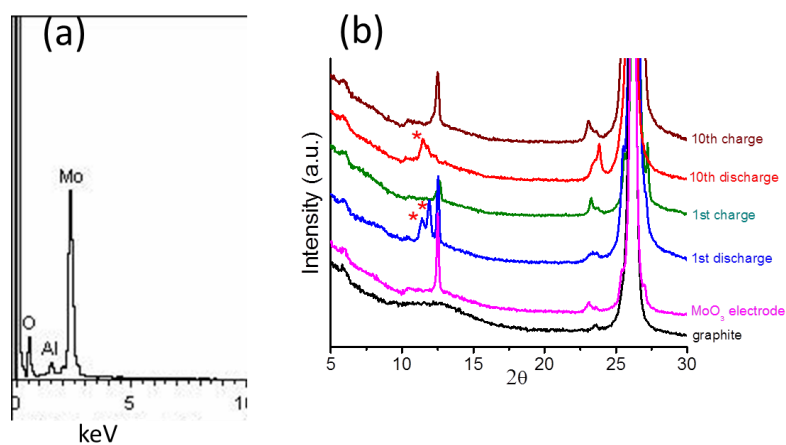


Figure 3. Energy dispersive X-ray (EDX) spectra of (a) 1st discharge state MoO₃ electrode and (b) Ex-situ XRD patterns of MoO₃ electrode before discharge, after 1st discharge, after 1st charge, after 10th discharge and after 10th charge (* corresponds to the emergence of additional peaks other than MoO₃.)

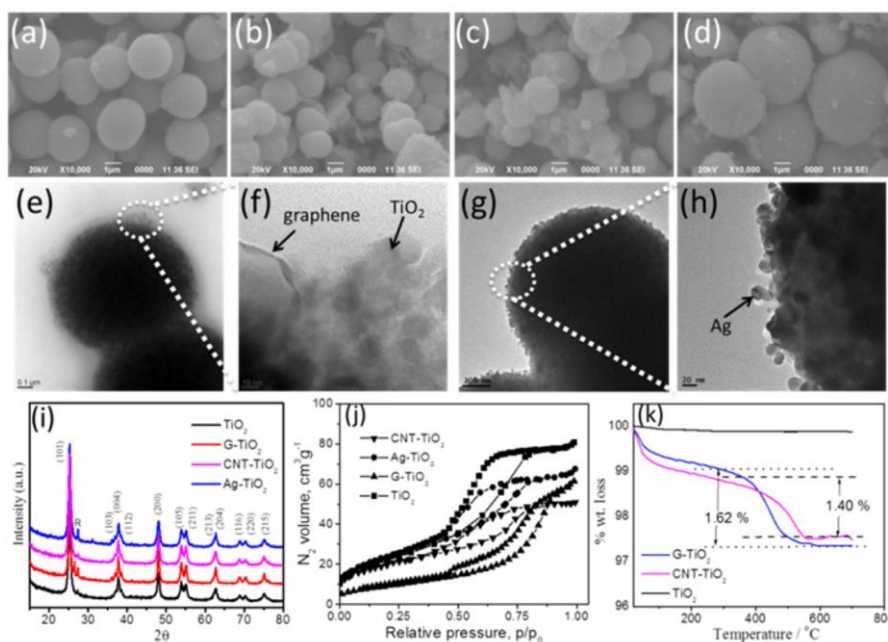


Figure 4. SEM micrographs of (a) TiO₂, (b) G-TiO₂, (c) CNT-TiO₂ and (d) Ag-TiO₂, TEM micrographs of (e, f) G-TiO₂ and (g, h) Ag-TiO₂, (i) XRD patterns, (j) N₂ adsorption/desorption isotherms, (k) Thermogravimetric analysis.

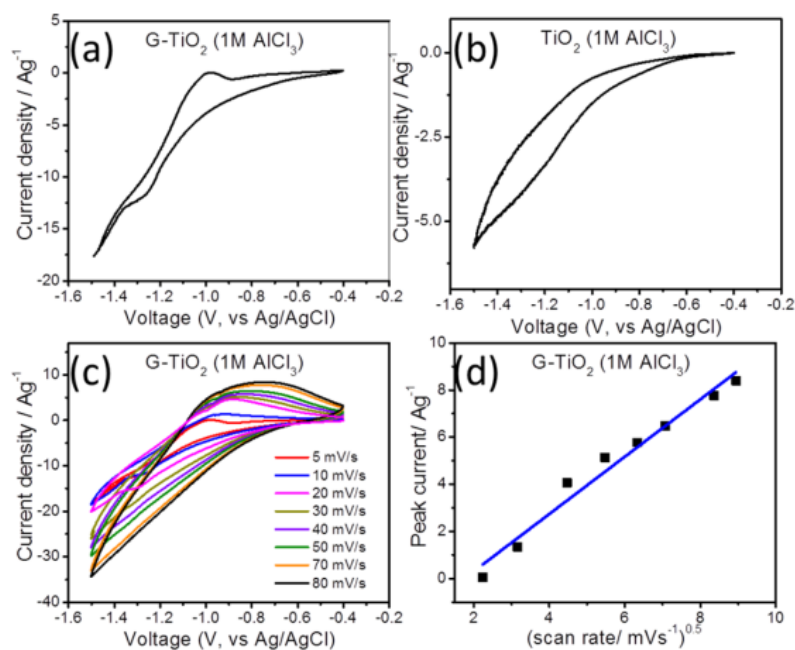


Figure 5. CV curves of (a) G-TiO₂ and (b) TiO₂ in 1 M AlCl₃ electrolyte at a scan rate of 5 mVs⁻¹, (c) CV curves of G-TiO₂ at different scan rates and (d) variation of redox peak currents versus scan rates according to equation $I = k\gamma^{0.5}$ (see text for detail). Anodic peak is considered here.

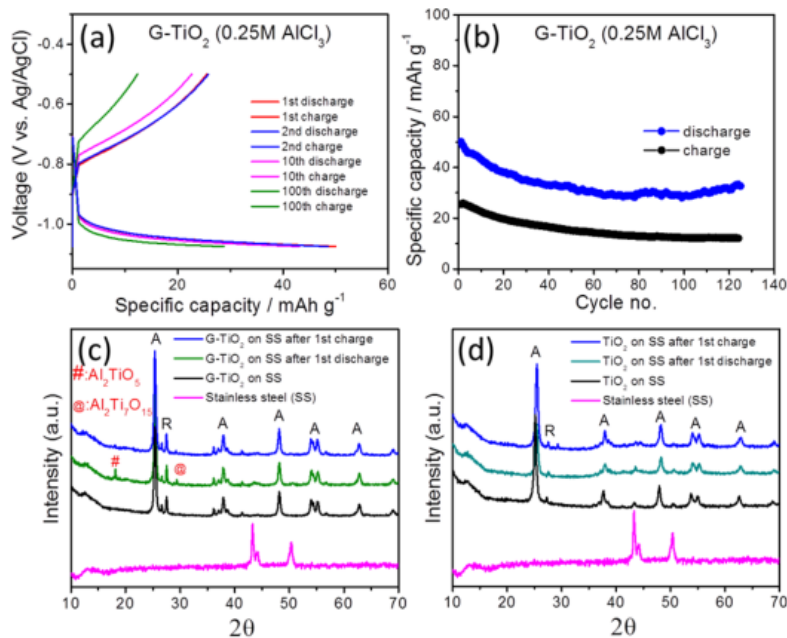


Figure 6. (a) Galvanostatic discharge/charge curves of G-TiO₂ at a current density of 6.25 Ag⁻¹ in 0.25 M AlCl₃ electrolyte at 25 °C and (b) respective variation of charge/discharge capacities with cycle number. Ex-situ XRD patterns before discharge, after 1st discharge and after 1st charge for (c) G-TiO₂ and (d) TiO₂.

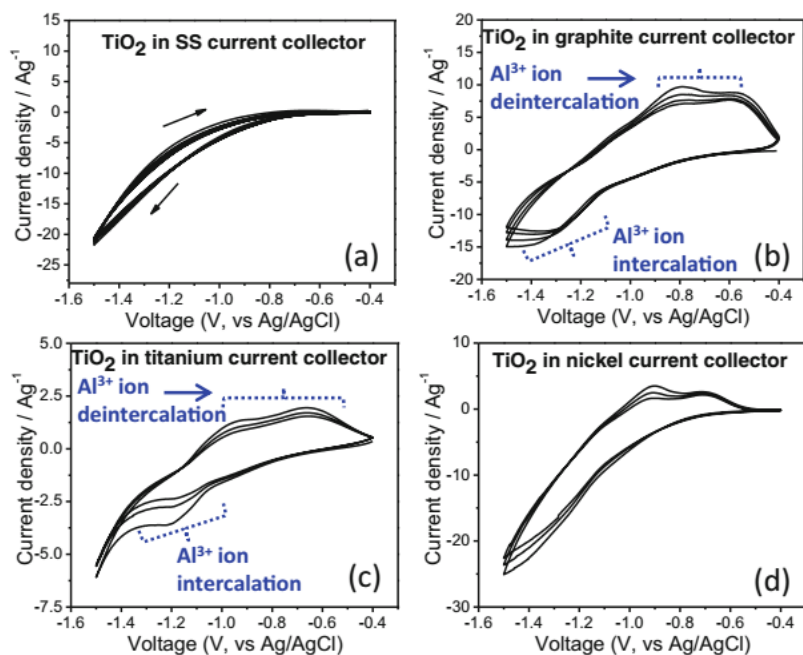


Figure 7 CV curves of TiO₂ particles with (a) stainless steel, (b) graphite, (c) titanium, (d) nickel current collectors.

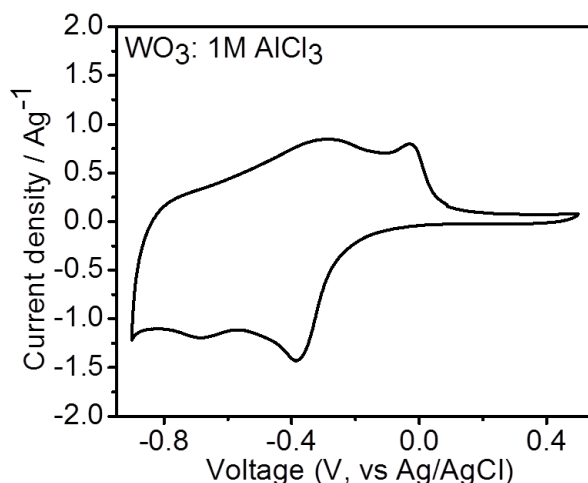


Figure 8 CV curves of graphene-WO₃

10. Detailed analysis of results indicating contributions made towards increasing the state of knowledge in the subject:

There are only few examples in the literature where Al³⁺ ion conducting aqueous electrolytes are used in ultracapacitors or batteries. Conventionally, the used aqueous electrolytes are KOH, LiOH, HCl, H₂SO₄ etc. We carried out all our investigations in Al³⁺ ion conducting aqueous electrolytes rather than using the conventional electrolytes and the outcomes are merely exciting. For instance, we found MoO₃ is electrochemically inert material in HCl, H₂SO₄ electrolyte. But it shows excellent electrochemical properties in Al³⁺

ion conducting aqueous electrolytes. For the first time, we report this Al^{3+} ion intercalation/deintercalation phenomenon in MoO_3 . Again, Al^{3+} ion intercalation/deintercalation process could be enhanced significantly by preparing graphene- MoO_3 nanocomposite. We also undertook work on TiO_2 . It was found that TiO_2 is an excellent host for Al^{3+} ion in aqueous medium. However, it was proved that TiO_2 is electrochemically active only when an appropriate current collector is used. Hence, we proposed for the first time that an appropriate current collector is a necessity for optimizing the performance of Al-ion capacitors or batteries. Moreover, we also noticed that a trace amount of graphene (< 2 wt%) could remarkably enhances the Al^{3+} ion diffusion coefficient in TiO_2 by 672 times.

11. Conclusions summarizing the achievements and indication of scope for future work:

The achievements are summarized in the following points.

(i) For the first time, we demonstrated that Al^{3+} ion conducting aqueous electrolyte could be used for MoO_3 /graphene- MoO_3 based electrode materials.

(ii) We also demonstrated the intricacies involved with TiO_2 /graphene- TiO_2 based electrode materials.

(iii) The proof for an appropriate current collector for optimizing the performance of aqueous electrolyte based Al-ion ultracapacitor or battery is also demonstrated.

Scope for future work:

Our work has opened up a completely new avenue in the area of aqueous ultracapacitors or batteries. We were able to introduce the concept of Al^{3+} ion conducting aqueous electrolytes for certain class of electrode materials. It is exciting and we are venturing into exploring other electrode materials based on our understanding on previous works. We are also in the process of making prototypes for Al^{3+} ion aqueous ultracapacitors or batteries.

12. S&T benefits accrued:

i. List of Research publications

Sl. No	Authors	Title of the paper	Journal	Volume	Pages	Year
1.	H. Lahan, S. K. Das	Al^{3+} ion intercalation in MoO_3 for aqueous aluminum-ion battery	Journal of Power Sources	413	134-138	2019
2	H. Lahan, R. Boruah, A.	Anatase TiO_2 as an anode material for rechargeable	J. Phys.	121	26241–	2017

	Hazarika, S. K. Das	aqueous aluminum-Ion batteries: remarkable graphene induced aluminum ion storage phenomenon	Chem. C		26249	
3	H. Lahan, S. K. Das	Active role of inactive current collector in aqueous aluminum-ion battery	Ionics	24	2175– 2180	2018
4	H. Lahan, S. K. Das	An approach to improve the Al ³⁺ ion intercalation in anatase TiO ₂ nanoparticle for aqueous aluminium-ion battery	Ionics	24	1855- 1860	2018
5	H. Lahan, S. K. Das	Graphene and diglyme assisted improved Al ³⁺ ion storage in MoO ₃ nanorod: steps for high- performance aqueous aluminum-ion battery	Ionics	25	3493- 3498	2019
6	S. K. Das, S. Mahapatra, H. Lahan	Aluminium-ion batteries: developments and challenges”	Journal of Materials Chemistry A	5,	6347	2017
7	S. K. Das	Graphene: a cathode material of choice for aluminium-ion battery	Angewandte Chemie Int. Ed.	57	16606– 16617	2018

ii. Manpower trained on the project

a) Research Scientists or Research Associates: NIL

b) No. of Ph.D. produced: 01

(Mr. H. Lahan, who was a JRF for this project, has submitted his thesis in June 2019)

c) Other Technical Personnel trained: 6 (MSc students who pursued projects)

iii. Patents taken, if any: Not yet

13. Financial Position:

No	Financial position/Budget	Funds Sanctioned	Expenditure	% of Total Cost
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	Head			
1	Salaries	484001	484001	17.46737956
2	Equipment	1231040	1231040	44.42768285
3	Supplies and materials	511646	511646	18.46507524
4	Contingencies	147803	147803	5.334144145
5	Travel	96395	96395	3.478852424
6	Overhead	300000	300000	10.82686578
7	Others	Nil	Nil	Nil
	Total			100%

14. Procurement/ Usage of Equipment

No	Name of Equipment	Make/Model	Cost	Date of installation	Utilization rate %	Remarks regarding maintenance
1	Electrochemical work station	Biologic SP300	Euro 15,473	26.07.2016	100%	In working condition
2	Tube furnace	Usha	Rs. 97,325/-	10.03.2016	100%	In working condition

b) Plans for utilizing the equipment facilities in future:

The Electrochemical work station is being extensively utilized to pursue other electrochemical research works beyond the proposed objectives in the proposal. Another PhD student joined under my supervision under institute fellowship in August 2018 and, hence the workstation is getting used for his research work. Additionally, MSc/BSc students who pursue projects under my supervision are also getting trained periodically to utilize the workstation for their research work. Overall, this equipment will be utilized for our research work in future.



15.07.2019

Name and Signature with Date:

Annexure-II

REQUEST FOR ANNUAL INSTALMENT WITH UP-TO-DATE STATEMENT OF EXPENDITURE

[For the Financial year 01.04.2018 to 24.11.2018]

1. SERB Sanction Order No and date: **FILE NO. YSS/2015/000765** Dated 04.11.2015
Diary No. SERB/F/3588/2016-17 Dated 30.08.2016
Diary No. SERB/F/5320/2017-2018 Dated 24.08.2017
Email received on 27th December 2018
2. Name of the PI : **Shyamal Kumar Das**
3. Total Project Cost : **Rs. 28,37,040/-**
4. Revised Project Cost : **N/A**
(If applicable)
5. Date of Commencement : **24-11-2015**
6. Statement of Expenditure :
(Month wise expenditure incurred during current financial year; 2018-2019)

Month and Year	Expenditure incurred (Rs)
April 2018	Nil
May 2018	16000
June 2018	16000
July 2018	16000
August 2018	16000
September 2018	16000
October 2018	16000
November 2018	21932
TOTAL	1,17,932

1. Grant received in each year:
 - a. 1st Year : **Rs. 17,66,373.00/-**
(Rs. 12,31,040.00/- (NonRecurring)+ Rs. 5,35,333.00/- (Recurring))
 - b. 2nd Year : **Rs. 5,35,000.00/-** (Diary No. SERB/F/3588/2016-17 on 30.08.2016)
 - c. 3rd Year : **Rs. 4,00,000.00/-** (Diary No. SERB/F/5320/2017-2018 24.08.2017)
 - d. Interest, if any : **Rs 69,512.00** [=Rs. 53,470 (1st yr) + Rs. 12,607(2nd yr) + Rs. 3435 (3rd yr)]
 - e. Total (a+b+c+d) : **Rs. 27,70,885.00/-**

Handwritten signature and date:
27/12-18

Annexure-II

Statement of Expenditure

(24.11.2015-31.03.2016, 01.04.2016-31.03.2017, 01.04.2017-31.03.2018 and 01.04.2018-24.11.2018)

Sr No (I)	Sanctioned Heads (II)	Total Fund Allocated (sanctioned) (1 st + 2 nd + 3 rd installments) (III) In ₹	Expenditure Incurred				Total Expenditure till 24.11.18(VIII) = IV + V + VI+VII) In ₹	Balance as on 24.11.2018 (IX = III - VIII) In ₹	Requirement of Funds upto 31 st March 2019	Remarks (if any)
			1 st (IV) (24.11.2015-31.03.2016)	2 nd (V) (01.04.2016-31.03.2017)	3 rd (VI) (01.04.2017-31.03.2018)	4 th (VII) (01.04.2018-24.11.2018)				
1.	Manpower costs	26,069.00	1,68,000.00	1,72,000.00	1,17,932.00	4,84,001.00	NIL		\$ As committed in 2016-2017, this amount is actually deducted from the Overhead of 2017-2018 since there was a negative balance of Rs. 45,876/- in 2016-2017	
2.	Consumables	(4,35,333.00 +4,35,000.00)	53,234.00	3,08,671.00	NIL	5,11,646.00	(Rs 1170333 + bank interest) -	NIL		
3.	Travel	+3,00,000.00) =	10,824.00	70,516.00	NIL	96,395.00	Rs. 1239845)			
4.	Contingencies	11,70,333.00	50,000.00	50,000.00	NIL	1,47,803.00				
5.	Others, If any		NA	NA	NA	NA				
6.	Equipment	12,31,040.00	NIL	12,76,916.00* [Additional Rs. 45876/- (=Rs. 1276916-Rs. 1231040) is funded by University]	45,876.00 ³ (this amount is transferred from the overhead of 2017-18 and refunded to University)	12,31,040.00 [#] # [= Rs.1276916-Rs. 45876]	NIL	NIL	@When Rs. 45,876/- is transferred and deducted by the university, the total expenditure in the 2 nd year becomes Rs 17,10,087.00/-	
7.	Overhead	(1,00,000.00 +1,00,000.00 +1,00,000.00) =	1,96,989.00	1,03,011.00* [= Rs 57135 + \$Rs. 45876]	NIL	3,00,000.00	NIL	NIL		
8.	Bank Interest	(53,470.00 +12,607.00 +3435.00) =	NIL	NIL	69,512.00** (it is spent in manpower and so not considered in total)	NIL	NIL	NA		
9.	Total	27,70,855.00/- (with bank interest)	2,38,668.00	7,04,198.00	1,17,932.00	27,70,855.00/-	NIL	NIL		

Signature of Principal Investigator
27.12.18

SHYAMAL KUMAR DAS

Signature of Competent Financial Authority with seal and date
28/12/18

Finance Officer
Tezpur University

UC for Non Recurring Grants

UTILISATION CERTIFICATE [FOR THE FINANCIAL YEAR – 01.04.2018 to 24.11.2018]

Final UC.

U.C pertains to
✓ appropriate box

First Release	Second Release	Third Release	Fourth Release	Final Release
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Is the UC provisional

: YES/NO

1. Title of the Project/ Scheme: "High performance ultracapacitors with graphene-based composite electrodes"

2. Name of the Principal Investigator : **Shyamal Kumar Das**

3. Implementing Institution : Tezpur University

4. SERB order No & date : **FILE NO. YSS/2015/000765** dated on 04.11.2015

5. Amount brought forward from the previous Financial year quoting SERB letter no and date in which the authority to carry forward the said amount was given

i. Amount : NIL

ii. Order No : Email received on 27.12.2018

iii. Date : 27.12.2018

6a. Amount received during the financial year; 2018-2019 (Please give SERB Sanction order no and date)

i. Amount : NIL

ii. Order No : Email received on 27.12.2018

iii. Date : 27.12.2018

6b. Interest earned, if any

: NIL

7. Total amount that was available for expenditure (excluding commitments) during the financial year; 2018-2019 (Sr. No. 5+6a+6b)

: NIL

8. Actual Expenditure (excluding commitments) Incurred during the financial year; (upto 24.11.2018)

: NIL

9. Balance amount available at the end of the financial year; 2018-2019 (7-8)/ OR **Negative balance** (if expenditure incurred is more than the funds released) : NIL

10. Unspent balance refunded, if any, refunded (please give details of cheque no etc.) : NIL

11. Amount to be carried forward to the next financial year (if any) : NIL


27.12.18

UTILISATION CERTIFICATE

[For the Financial year 01.04.2018-24.11.2018]

Certified that out of Rs. NIL of Non Recurring grants-in-aid sanctioned during the year 2018-2019 in favor of The Registrar, Tezpur University, Tezpur-784028, Assam and a sum of Rs. NIL has been utilized for the purpose of Research for which it was sanctioned.

Certified that we have satisfied ourselves that the conditions on which the grants-in-aid was sanctioned have been fulfilled/are being fulfilled and that we have exercised the following checks to see that the money was actually utilized for the purpose for which it was sanctioned.

Kinds of checks exercised:

1. *Stock verification*
- 2.


Signature of PI

Date: 27.12.18


Signature of Registrar/
Head of the Institute
Registrar
Date:
Tezpur University


Signature Accounts Officer
Finance Officer
Date:
Tezpur University

Science and Engineering Research Board

UC has been accepted by

Signature: _____
Name of the SERB Officer: _____
Designation: _____

UTILISATION CERTIFICATE
[FOR THE FINANCIAL YEAR – 01.04.2018 to 24.11.2018]

U.C pertains to
 appropriate box

First Release	Second Release	Third Release	Fourth Release	Final Release

Final UC

Is the UC provisional : YES/NO

1. Title of the Project/ Scheme: “High performance ultracapacitors with graphene-based composite electrodes”
2. Name of the Principal Investigator : **Shyamal Kumar Das**
3. Implementing Institution : Tezpur University
4. SERB order No & date : **FILE NO. YSS/2015/000765** dated on 04.11.2015
5. Amount brought forward from the previous Financial year quoting SERB letter no and date in which the authority to carry forward the said amount was given
 - i. Amount : Rs. 1,17,932.00/-
 - ii. Order No : Email received on 27.12.2018
 - iii. Date : 27.12.2018
- 6a. Amount received during the financial year; 2018-2019 (Please give SERB Sanction order no and date)
 - i. Amount : NIL
 - ii. Order No : Email received on 27.12.2018
 - iii. Date : 27.12.2018
- 6b. Interest earned, if any : NIL
7. Total amount that was available for expenditure (excluding commitments) during the financial year; 2018-2019 (Sr. No. 5+6a+6b) : Rs. 1,17,932.00/-
8. Actual Expenditure (excluding commitments) Incurred during the financial year; 2018-2019 (upto 24.11.2018) : Rs. 1,17,932.00/-
9. Balance amount available at the end of the financial year; 2018-2019 : NIL
(7-8)/ OR Negative balance
10. Unspent balance refunded, if any, refunded (please give details of cheque no etc.) : NIL
11. Amount to be carried forward to the next financial year (if any) : NIL

[Signature]
 27-12-19

UTILISATION CERTIFICATE

[For the Financial year 01.04.2018 to 24.11.2018]

Certified that out of Rs. NIL of Recurring grants-in-aid sanctioned during the year 2018-2019 in favor of The Registrar, Tezpur University, Tezpur-784028, Assam vide email dated 27.12.2018 and Rs. 1,17,932.00/- on account of unspent balance of the previous year (2017-2018), a sum of Rs. 1,17,932.00/- has been utilized till 24.11.2018 for the purpose of Research for which it was sanctioned.

Certified that we have satisfied ourselves that the conditions on which the grants-in-aid was sanctioned have been fulfilled/are being fulfilled and that we have exercised the following checks to see that the money was actually utilized for the purpose for which it was sanctioned.

Kinds of checks exercised:

1. *stock verification*
- 2.


Signature of PI

Date: 27-12-18


Signature of Registrar/
Head of the Institute
Registrar
Tezpur University
Date:


Signature Accounts Officer
Finance Officer
Tezpur University
24/12/18

Science and Engineering Research Board

UC has been accepted by

Signature: _____
Name of the SERB Officer: _____
Designation: _____