A New Graphene Composite With A High Coulombic Efficiency

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Abstract

Zinc-graphene composite has been electrolytically produced for the first time using a graphene quantum dot (GQD) electrode. The electrochemical reduction of zinc ion at a GQD electrode is shifted to a lesser negative potential with the complimentary anodic peak due to the oxidation of the composite shifted towards a positive potential as compared to zinc ion reduction in the GQD bath. The coulombic efficiency of the composite represents a gain of nearly 10% over the conventional Zn/Zn²⁺ in the energy storage systems. In galvanostatic electrolysis, the deposition of zinc-graphene composite is carried out under neutral and acidic conditions. The X-ray diffraction of the electrolytically prepared composite shows distinct features of 2 theta reflection at 8° due to (001) plane of graphene, in addition to the characteristic reflections at 38.9°, 43.2°, 54.3°, 70.1° and 90° arising from Zn at (002), (100), (101), (102) and (110). A large scale preparation of the zinc-graphene composite has been achieved at a zinc plate as the working electrode in the GQD bath. The composite is stable up to 250°C. Scanning electron microscopic (SEM) and energy dispersion X-ray analysis (EDAX) shows a string like structure with peaks for carbon and zinc in EDAX.

Keywords: Graphene quantum dot, Zinc, SEM, EDAX, zinc-graphene composite.

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GRAPHICAL ABSTRACT

1. Introduction

Zinc occupies twenty third position among the elements available (0.013 wt%)[1] on earth and is widely used in a large number of applications such as drainage, architectural roofing, galvanic protection and devices. It is environmentally suitable and hence is the most preferred material by the designers and architects. The composites of zinc have been very useful in several technological applications such as durability, bending strength, flatness and workability and anti fouling [2].

The electrochemical deposition of zinc is of great importance in the construction of energy storage devices [3-16] as zinc has a large negative potential that permits the reach of high voltage and high energy density in batteries when it is coupled with other redox couples. The earliest successful primary battery is the Daniel cell that utilizes zinc with its ions and copper with its ions as the redox couples. This triggered the development of a large number of energy storage batteries such as zinc-air battery, zinc-chlorine battery, zinc-bromine battery and zinc-nickel battery having theoretical specific energy in the range of 54-1370 Wh/kg [3,9,10,12,61,64]. In the process of the operation of the energy storage devices involving zinc, the operational cycle involves its dissolution and redeposition except in the Daniel cell where only dissolution of zinc occurs. Recently, a modified Daniel cell has been proposed where dissolution and redeposition is carried out [13]. In this cycle, dendritic growth of zinc and the shorting of the battery occurs in a large number of zinc batteries leading to their restricted usage. This problem is encountered with other metals such as copper and has been researched to control the dendrite formation [14]. Zinc redox couple has also found usage in light weight conducting polymer batteries [15,16].

In the literature [17-19] the electrodeposition of zinc is carried out in acid solutions containing chloride or sulfate on a variety of substrates such as mild steel, copper, etc.[20]. Among other deposition baths, cyanide and fluoroborate baths have been widely used successfully [20,21]. Due to toxicity of cyanide, the bath disposal requires additional treatment procedures. This has resulted in the development of non-cyanide baths [22,23] as cyanides are toxic that enforces an environmental pollution control.

Graphene and its metal composites are of importance in a number of applications such as energy storage devices, sensors, flexible electronics, LED lighting, solar cell and battery super capacitors, flexible display touch panel, high speed transistor, conductive ink and chemical sensors. The metal composites have potential applications in hydrogen storage and automobile and airplane components. A literature survey shows that graphene has been combined with zinc oxide by plasma enhanced chemical vapor deposition [24], thermal decomposition [25] and electrohydrodynamic atomization [26] and solvothermal method [27]. This results in the formation of graphene-zinc oxide composite. While this type of composite is useful for solar energy storage, such composites have very limited applications in other energy storage systems. For several other energy storage systems such as batteries the zinc composites have provided greater stability and performance [3]. We wish to report here a novel method of preparing nanosized string like zinc-graphene composite using GQD bath that shows potentiality for near 100% charge storage and recovery. In addition, we compare the characteristics of the zinc ion reduction on immobilized GQD electrode with its reduction in the GQD bath through current-time transients for recognizing the type of nucleation process in forming the composite. The GQD bath studied here makes it conducive for the deposition of the composite on metal plates such as zinc.

2. MATERIALS AND METHODS

2.1. Chemicals

Zinc sulfate, potassium ferrocyanide, sodium sulfate were procured from Aldrich Chemical Company. Graphene quantum dot (GQD) was prepared as per the procedure reported [28] and stored in a amber colored bottle. TTK-4 graphite plate was used in the preparation of graphene and was supplied by Ohio carbon Black. Argon gas (99.99% pure) cylinder was obtained from Linde, Fulton, NY.

2.2. Instruments

Gamry electrochemical instrument was used in the measurements. Bob's cell was used the electrochemical measurements. A saturated calomel electrode (SCE) was used as the reference electrode. Electrodes: Pt disc ($A=0.0766\text{ cm}^2$), graphite rod (diam.0.5 cm, Length 6 inch), glassy carbon electrode (Gamy Instrument) ($A=0.0750\text{ cm}^2$) were used as appropriate for the measurements. Glassy carbon electrode was deposited with GQD (5% w/v; 5 -100 nm) following

the method described in a previous publication [29]. The electrode is characterized for the area by recording the cyclic voltammetry of 10.47 mM K₄Fe(CN)₆.

2.3. Electrodeposition of zinc-graphene composite

All the studies were carried out either in A) aqueous sulfate bath or B) GQD bath. The aqueous sulfate bath was made using 0.1 M sodium sulfate. The bath may have sulfuric acid added when electrodeposition is carried out at low pH in some experiments. The GQD bath contains 0.1 M sodium sulfate along with graphene quantum dot. For large scale deposition for scanning electron microscope recordings, the solution composition used was a mixture of zinc sulfate (0.6 M), sodium sulfate (0.1 M) and GQD for 90 s or 900 s deposition. The solution pH was adjusted to 1.6. In galvanostatic electrolysis, the current density was maintained at 300 mA/cm². All experiments were carried out under argon gas atmosphere after degassing the solution.

2.4. Thermogravimetric measurements

TGA measurements were carried out using TA-Q500. A platinum pan is used for the experiments. The temperature was ramped at 5°C/min from ambient to 800°C. The experiments were carried out by passing purified air from a cylinder.

2.5. Quantum dots

Scanning electron microscope (SEM) and Transmission Electron Microscope (TEM) were used for characterizing samples. Images and selected-area diffraction patterns were obtained in either a JEOL 2000FX or a 100CX TEM, both with tungsten filaments. Image magnification was calibrated using phase-contrast images of asbestos fibers. High resolution (HRTEM) images were obtained on a JEOL JSM-6460 LV. Energy dispersive spectrum is made by Thermo Scientific. It is equipped with an UltraDry detector and NSS software. The images were recorded on Kodak 4489 electron microscope film and digitized with a Nikon 9000 film scanner.

3. RESULTS AND DISCUSSION

In order to arrive at the conditions required for the electrochemical deposition of zinc-graphene composite, experiments were carried out in aqueous sulfate and acid electrolytes containing GQD, using cyclic voltammetry, chrono amperometry and differential pulse voltammetry. Figure 1 shows the cyclic voltammetric curve of zinc ion reduction in GQD bath that results in the formation of zinc-graphene (Zn-GQD) composite on glassy carbon electrode by reaction (1)

that is followed by oxidation process of removal of the deposit by reaction (2).

Figure 1. Cyclic voltammetry of 4.37 mM zinc ion in GQD bath.

Table 1. Zinc ion reduction in GQD bath

Sweep Rate, V/s	ΔE_{pc}^I (mV)	R_1 (uA)	ΔE_{pa}^I (mV)	R_2 (uA)	$\Delta E_{p/2}$	R_3
0.02	40	1.25	30	1.04	0.026^1 0.061^2	0.81^2 0.79^2
0.05	30	1.32	30	1.32		
0.10	30	1.25	40	1.25		
0.20	31	1.20	30	1.20		

$\Delta E_{pc} = (E_{pc}^{Zn^{2+}} - E_{pc}^{Zn^{2+}-GQD})$; $\Delta E_{pa} = (E_{pa}^{Zn^{2+}} - E_{pa}^{Zn^{2+}-GQD})$; R_1 = Ratio of Cathodic peak currents for Zinc ion reduction in GQD to aqueous baths. $\Delta E_{p/2} = (E_{pc} - E_{p/2c})$; 1:Aqueous bath 2:GQD bath R_3 : Ratio of cyclic voltammogram integrated anodic peak to the cathodic peak areas.

The reduction of zinc ion in this bath is contrastingly different from the aqueous bath with no GQD; the cathodic peak potential is shifted anodically at all sweep rates and the cathodic peak currents are higher in the GQD bath. Table 1 shows the magnitude of the differences observed at different sweep rates. The cyclic voltammetric peaks are characterized by different ways [30]; one way to characterize the peak is by examining the magnitude of the difference between peak

and half peak potentials. For a truly reversible one electron reduction the expected difference is 59 mV [30]. When the zinc ion reduction is carried out in GQD bath, this difference is 61 mv (Table 1). The shift in peak potential from the aqueous bath, taken along with the above difference suggests there is binding of GQD to the deposited zinc (see XRD discussion). The cyclic voltammetric feature shows no evolution of hydrogen is observed at the cathodic potential of -1.2 V as at this potential when the glassy carbon electrode is deposited with zinc, one would expect hydrogen ion reduction to follow on this surface. Zinc deposition potential based on its standard potential is less negative than hydrogen ion reduction in the GQD bath. Zinc nucleation interestingly occurs depending on the medium at different potentials on different electrodes. At stainless steel electrode zinc nucleation is observed at -0.80 V vs SCE [31] and the nature of the deposits as a function of the exchange current density [32], anions in solutions [33-35] and temperature [36,37] have been discussed in the literature. These factors also influence the morphology of the zinc deposits. The cyclic voltammetric peak potential difference of 30 mV between anodic and cathodic peaks for zinc ion reduction in the GQD bath (Figure 1) is indicative of a reversible 2e- process. In comparison the electron transfer reaction in methane sulphonic acid bath is quasi reversible [38] with peak potential difference of 160 mV and 100-150 mV in chloride and sulfate electrolytes respectively. The charge ratio of the two peaks runs in the range of 79-81% [38].

3.1. Diffusion coefficient of Zn^{2+} in GQD Bath

Using the Ficks's diffusion model and the boundary conditions appropriate for cyclic voltammetry (30), the diffusion coefficient of zinc ion is related to the peak current as shown below

$$D^{1/2} = [i_p / (2.65 \times 10^5) n^{3/2} A C^* v^{1/2}] \quad (3)$$

where D is the diffusion coefficient of zinc ion, i_p is the cathodic peak current, n is the number of electrons, A is the area of the electrode, C^* is the zinc ion concentration in solution and v is the sweep rate (V/s). Taking the average value of six measurements, the diffusion coefficient of zinc ion is calculated as $D_{zn^{2+}} = 4.19 \times 10^{-6} \text{ cm}^2/\text{s}$ at 23°C. It is interesting to compare the diffusion coefficient of zinc ion that has been reported in the literature by Cathro [39]. At 30°C, the diffusion coefficient in sulfate bath having a kinematic viscosity of $1.53 \text{ m}^2/\text{s}$ is reported as 4.7

$\times 10^{-10} \text{ m}^2/\text{s}$ (equivalent to $4.7 \times 10^{-6} \text{ cm}^2/\text{s}$). We measured the viscosity and density of the solutions that were used in the cyclic voltammetric experiments by conventional methods using viscometer and densitometer; the values obtained are $0.87 \text{ m}^2\text{s}^{-1}$ and 1.188 g/cm^3 . There are other reports of diffusion coefficient measurements of zinc ion at 25°C ; using non-electrochemical method such as Rayleigh optics, Albright and Miller [40] obtained diffusion coefficient that is dependent on the electrolyte (ZnSO_4 concentration); at 0.004 M , the value is $8.48 \times 10^{-6} \text{ cm}^2/\text{s}$ and in 3.33 M concentration it is $2.81 \times 10^{-6} \text{ cm}^2/\text{s}$. Using a mercury electrode as the working electrode, El-Hallag [41] reported in chloride medium a diffusion coefficient value of $2.44 \times 10^{-6} \text{ cm}^2/\text{s}$ at 25° . In another report [42], the diffusion coefficient is measured as $7.03 \times 10^{-6} \text{ cm}^2/\text{s}$ in potassium nitrate solution at 25°C . In 10% ethanol containing potassium nitrate, the D value changes to $6.19 \times 10^{-6} \text{ cm}^2/\text{s}$. Using radioactive label under electric field created by LiCl [43] the diffusion coefficient for Zn salts are listed in the range of $6.54\text{--}6.77 \times 10^{-6} \text{ cm}^2/\text{s}$. Interestingly, the electrochemical techniques have always yielded lower values ranging from $1.51\text{--}3.35 \times 10^{-6} \text{ cm}^2/\text{s}$ [44]. Considering all the reports in the literature, it is apparent that the diffusion coefficient of zinc ion is in the range of $1.51\text{--}8.48 \times 10^{-6} \text{ cm}^2/\text{s}$ due to the different conditions and techniques used for the measurement. It is significant to note that the diffusion coefficient value obtained by electrochemical techniques are in the range of $1.51\text{--}4.7 \times 10^{-6} \text{ cm}^2/\text{s}$; while at mercury electrode the value obtained is lower than the glassy carbon electrode. This difference shows the processes occurring are different; metal amalgam formation with Hg electrode and metal deposition at glassy carbon electrode here. In addition to it there is a spherical diffusion that occurs at mercury drop electrode to semi infinite linear diffusion at glassy carbon electrode. In order to get further insight into the diffusion process that occurs at glassy carbon electrode, we have examined the electrochemical reduction of zinc by potential step electrolysis. Based on the slope of the plot i vs $t^{-1/2}$, the diffusion coefficient is calculated as $4.20 \times 10^{-6} \text{ cm}^2/\text{s}$ (Figures 2A and 2B). The value obtained here agrees very closely with the cyclic voltammetric data. In GQD bath the diffusion

Figure 2. A: Current-time curve obtained in potential step electrolysis at -1.45 V at glassy carbon electrode B: Cottrell's plot. GQD Bath. C: Current-time curve obtained in potential step electrolysis at -1.45 V at GQD electrode. D: Cotrell's plot.

coefficient value obtained is $9.67 \times 10^{-6} \text{ cm}^2/\text{s}$ which is higher than the aqueous bath. With GQD bath, the graphene particles are in constant motion in the solution that produces the accelerated diffusion. Bard and coworkers [45] have shown that nanoparticles tend to be in constant motion in solution that results in collisions with an ultra micro electrode. A similar situation exists with GQD bath where the motion of these particles results in the collision with the zinc ions in solution. This movement is removed at the GQD electrode described in the next section.

3.2. Measurements on GQD electrode

Cyclic voltammetry of potassium ferrocyanide is used as a bench mark for the calibration of the electrochemical area of the GQD coated electrode. In Figure 3A, the cyclic voltammetric curves of $\text{K}_4\text{Fe}(\text{CN})_6$ are shown at different sweep rates which exhibits the peak current increasing with sweep rate. Figure 3B depicts the plot of peak current with sweep rate. The effective area was calculated using the diffusion coefficient of the ferrocyanide ion reported in

the literature [30] using the peak current value in the calculation. The cyclic voltammetric curve for ferrocyanide ion at a GQD working electrode showed higher currents which resulted in 1.71 times increase in the effective area of the GQD electrode over glassy carbon electrode. At GQD

Figure 3. A. Cyclic voltammetric curve of 10.47 mM $K_4Fe(CN)_6$ in 0.1 M Na_2SO_4
B. Plot of peak current vs sweep rate at GQD coated glassy carbon electrode.

electrode, the peak current increased with sweep rate as shown in Figure 3B, as expected from the cyclic voltammetric peak current equation [30]. At GQD electrode the zinc ion reduction occurs as shown in Figure 4. The peak potential difference between the anodic and cathodic

peaks, the peak current ratio and the current function values of anodic and cathodic peaks are similar to the one obtained in GQD bath. The cathodic peak is observed at the same potential as seen with glassy carbon electrode except the peak current is higher than at a glassy carbon electrode. The anodic peak is shifted towards the potential observed in the GQD bath ($E_{pa} = -1.03$ V). The electrochemical reduction of hydrogen ion to hydrogen occurs at about -1.45 V at this electrode based on the experiments carried out with background electrolyte alone.

Figure 4. Cyclic voltammetry of 5 mM zinc sulfate in aqueous bath. Inset shows the GQD coated electrode used in the experiment.

3.3. Coulombic efficiency

The linear sweep voltammetry and potential-step electrolysis have been used to examine the charge storage and recovery ability. Table 2 gives the charge passed and charge recovered. The charge ratios of near 100% is achieved at GQD electrode suggesting that the composite stability is higher than in the GQD bath. Preliminary studies showed that the charge stored material recovers efficiently even after 24 hours. The performance of GQD electrode opens up the prospects of its usage in redox flow batteries. Currently, with these batteries the maximum reported charge recovery with Zn/Zn^{2+} is 90% which in comparison with the composite studied

here is less by 10%. The flow batteries have been widely considered for power grid applications [46] involving the use of two redox couples having high solubilities [47]. Among the flow

Table 2. Coulombic Efficiency of Zn-graphene Compoiste.

Charge Passed, mC	Charge Recovered, mC	Charging time,s	Efficiency
1.401	1.399	37.0	99.86
1.403	1.400	18.5	99.88
1.401	1.405	7.4	100.00
1.500	1.499	3.7	99.93

batteries, Zn/Zn^{2+} couple in combination with other redox couples is playing an important role; however, the redox process associated with zinc metal has a problem that is similar to what occurs in batteries; the redeposition of zinc ion from the medium results in dendrite growth that results in a reduced performance with time. The dendritic growth in the redistribution of zinc has been observed at low current densities of $15\text{mA}/\text{cm}^2$ [38] and it increased with increasing current densities. This has resulted in the poor performance of the flow battery. With Br_2/Br^- couple in combination with Zn/Zn^{2+} , the flow battery is estimated to give 1.8 V with a theoretical specific energy of 429 Wh/kg that is seldom realized. In practice, the flow battery gives 65 Wh/kg [46] and gives a round trip energy efficiency of 65-75%. To overcome the dendritic formation the additives such as methane sulfonic acid have been used. Banik and Akolkar [48] used polyethylene glycol as an additive to suppress the dendritic growth and examined the kinetic parameters operating in this suppression. Lueng et al [38] claimed charge efficiency of 91% by using methane sulfonic acid as additive. In the present work, a higher efficiency of near 100% has been obtained with zinc-graphene composite using the GQD electrode with no dendrite formation (see SEM section).

3.4. Modeling Nucleation of Zinc-graphene Composite

The 3D growth of zinc during electrodeposition has been previously investigated by a number of workers in acid and alkaline medium using theoretical models [49,50]. The theoretical

models show divergent behaviors for instantaneous and progressive nucleations which are described by non-dimensional equations (4) and (5)

$$(i/i_m)^2 = [1.9542/(t/t_m)] \{1 - \exp(-1.2564 (t/t_m))\}^2 \quad (4)$$

and

$$(i/i_m)^2 = [1.2254/(t/t_m)] \{1 - \exp(-2.3367 (t/t_m)^2)\}^2 \quad (5)$$

The theoretical model defines the expected maximum current and the time at which it is reached by the following expressions for instantaneous case

$$t_m = \{1.2564/N_o\pi K D\} \quad (6)$$

$$N_s = \{1.2564/t_m\pi K D\} \quad (7)$$

Figure 5. Plot of $(i/i_m)^2$ vs (t/t_m) in GQD bath and GQD coated electrode.

and

$$i_m = 0.6382 n F D C (K N_o)^{1/2} \quad (8)$$

The corresponding equations for progressive nucleation are

$$t_m = \{4.6733/\pi A N_o D K\}^{1/2} \quad (9)$$

$$N_s = \{A N_o / 2 K D\}^{1/2} \quad (10)$$

$$\text{and } i_m = 0.4615 n F D^{3/4} C (K A N_o)^{1/4} \quad (11)$$

where n is the number of electrons in the reduction of zinc ion, F is the Faraday, D is the diffusion coefficient of zinc ion, t is the time of electrolysis in seconds, N_o , N_s are the number density of nucleation sites, A is the steady state nucleation rate and K is growth rate constant of nucleus given by

$$K=[8\pi CM/\rho]^{1/2} \quad (12)$$

where C is the zinc ion concentration and M is molar mass and ρ is the density. With the data obtained in potential step electrolysis at $-1.45V$; $t_m=0.04s$, $i_m= 2.3 \times 10^{-4}A$, $D= 9.67 \times 10^{-6}cm^2/s$, $M= 65.38 \text{ g/mole}$, $\rho =7.14 \text{ g/cm}^3$ and $C=4.54 \text{ mM}$ in the GQD bath, $N_s=3.0 \times 10^7$ (instantaneous) and $N_o= 0.78 \times 10^5$ (progressive) have been obtained. Figure 5 gives the observed features of the plot of $(i/i_m)^2$ vs (t/t_m) for zinc-graphene composite at glassy carbon electrode in GQD bath and the composite formation at the GQD electrode. The observed features at GQD electrode fit well into progressive nucleation; the theoretical model [49-51] predicts a faster decay of current ratio than in the instantaneous nucleation. It appears that in the GQD bath the zinc-graphene composite follows an instantaneous nucleation.

Interaction of GQD with Zinc ion:

The GQD fluorescence has been studied previously [52-56] in detail; when the GQD solution is excited at $\lambda=360 \text{ nm}$, the fluorescence spectrum shows a maximum at $\lambda=440 \text{ nm}$. The life time of the excited state of GQD has been reported as 6.77 ns [52]. The fluorescence of GQD is quenched by metal ions like cupric ion [16]. With a view to understand the zinc ion interaction with GQD, the fluorescence intensity of GQD is measured at different concentrations of zinc ion in the solution. Table 3 shows the fluorescence intensity as a function of zinc sulphate concentration and the decreasing magnitude of the intensity with zinc sulfate concentration. The decrease in intensity is attributed to collisional quenching of GQD fluorescence by zinc ion. This result demonstrates that there is interaction between GQD and zinc ion in solution.

3.5. Thermogravimetric analysis (TGA) of zinc-graphene Composite

A large scale preparation of the composite is carried out using a zinc plate working electrode and a large zinc foil rolled into a cylinder as the counter electrode. By carrying out a galvanostatic electrolysis, the material deposited on the working electrode is collected, washed

Table 3. GQD Fluorescence Quenching by ZnSO₄

Concentration of ZnSO ₄ , mM	I	I _f /I _o
0	0.78	1.00
0.01	0.65	0.83
0.10	0.62	0.79
1.00	0.58	0.74

I_o = Fluorescence intensity of GQD and

I_f= Fluorescence intensity in the presence of ZnSO₄.

and dried at 80°C for two hours. The composite is examined by TGA at 5°C ramp from a temperature range of 25°C to 400°C. Figure 6 gives the TGA of the composite that shows a

Figure 6. TGA of Zinc-GQD composite made electrolytically.

small initial weight loss up to 120°C due to moisture that is followed by a sharp loss of weight followed by levelling. This transition is attributed to the break down of the composite to Zn. The mass of zinc in the composite has been determined by this method. In a typical experiment, 4.728 mg of the composite gave 4.288 mg of zinc (after removing the moisture content in the sample). By subtracting the mass of zinc from the net dry weight of the composite, the GQD content was obtained. If we continue the TGA experiment beyond 450°C, there is weight gain is observed due to oxidation of zinc that results in ZnO [57].

3.6. XRD Features of Zinc-graphene Composite

The electrochemically deposited zinc-graphene composite is characterized by its XRD features (Figure 7). It showed 2θ reflections at 8° , 38.9° , 43.2° , 54.3° , 70.1° and 90° which are attributed to graphene and zinc (100), (101), (102), (103) and (110) phases (JCPDS Card Number 87-0713). An interesting feature of the zinc-graphene composite is that the most intense peak is

Figure 7. XRD of electrolytically prepared zinc-graphene composite.

located at 70.1° corresponding to (110) plane where as in zinc the most intense peak is at 43.2° that represents (101) plane. Note the absence of two theta reflections at 48° , 57° and 63° which are characteristic reflections for zinc oxide demonstrating its absence in the composite.

3.7. Scanning Electron Microscopic and Energy Dispersion Analysis

The electrolytically prepared zinc-graphene composite was mounted on Al stubs using silver paint to make electrical contact and secure the sample to the stub. The individual stubs were attached to a large sample holder using silver paint. The use of silver paint prevents any contamination coming from other sources. The surfaces were analyzed and imaged for understanding the growth of the composite. The SEM of the zinc-GQD composite is shown in Figure 8. The composite shows a string like structure with no dendritic growth. The EDXA spectrum shows that the Zn-graphene composite has Zn, C and O as the elemental composition. By comparing the XRD data described in the earlier section with the EDXA data, it appears that the O is associated with graphene and not with the zinc atom based on the following reasons. A) the XRD spectrum of the Zn-graphene composite does not show peaks due to ZnO at 31.7° and 62.5° due to (100) and (103) planes [58,59] B) The XRD spectrum shows a peak at 10° that is attributed to graphene oxide suggesting carbon and oxygen are bonded.

Figure 8. A) SEM of electrolytically prepared Zn-graphene sample B) EDAX of the same sample.

3.8. Efficient Energy Storage System

A large number of reports [3-12] on energy storage systems involving Zn/Zn²⁺ redox couple show that it is a low cost, light weight, high specific capacity, high energy density with an additional advantage of free from pollution and high safety. For zinc-air storage system the expected theoretical capacity and energy densities are 820 mAh/g and 1312 Wh/kg and for zinc-bromine system, the corresponding values are 238 mAh/g and 428 Wh/kg with nearly one seventh of the energy density practically being realized [48]. With these systems a charge ratio of 0.80-0.90 has been accomplished. Due to high negative potential of this couple, it provides an advantage of achieving a high open circuit voltage. Zinc batteries are used in a number of applications involving communications. Currently there is demand to improve their performances especially with regard to durability and coulombic efficiency [60-70]. As this kind of energy storage systems are considered for green grid applications, any improvement that results in a better performance would be a bonus [71-73]. With zinc redox systems the cause for the charge ratio of less than unity has been analyzed and is attributed to the zinc deposition process in the charge/discharge cycles. Due to the very negative potential required for the deposition process, there is a slow concurrent reduction of hydrogen ion as a competing process that causes the coulombic efficiency to be lower. In the present study, at the GQD electrode, the reduction of zinc ion is shifted anodically (see Figure 4 and Table 2) thereby inhibiting the hydrogen evolution during the charging process. As a result, the charge ratio of unity (see earlier section on GQD electrode) has been achieved at the GQD electrode where zinc-graphene composite is formed through progressive nucleation process.

4. Conclusions

Zinc-graphene composite has been made by using GQD electrode and also by using GQD bath. The composite shows high charge storage and recovery that is amenable for use in redox storage batteries. The nucleation process has been analyzed from the current-time transients which show that there is difference in nucleation process on GQD electrode and in GQD bath. This is interpreted as due to constant agitation occurring due to kinetic movement of GQD particles. TGA analysis shows that the break shown of the composite occurs at 250°C with loss of weight, followed by weight increase beyond 450° due to the formation of zinc oxide. XRD analysis shows the presence of identifiable zinc phases in the composite along with graphene.

The fluorescence of GQD is quenched by zinc ions suggesting a collisional interaction with GQD resulting in the loss of energy.

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References

1. B. Mason, Principles of Geochemistry, Wiley, New York, NY (1952).
2. G. Wang, L.H. Liu, W. Li, Zinc-graphite composite coating for anti-fouling application, Materials Letters 65(2011) 3095-3097.
3. Z. A. Weber, M. M. Mench, J. P. Meyers, P. N. Ross, J. T. Gostick, Q. Liu, Redox flow batteries: A review, J Appl. Electrochem. 41 (2011) 1137-1164.
5. J.A. Kosek, A.B. Laconti, Advanced hydrogen electrode for hydrogen-bromine battery, J. Power Sources 22 (1988) 293-299.
6. A.Z. Weber, J. Newman, Modeling transport in polymer-electrolyte fuel cell Chem. Rev. 104 (2004) 4679-4726.
7. Q. Liu, A.A. Shinkle, Y. Li, C.W. Monroe, L.T. Thompson, A.E.S. Sleightholme, Non-aqueous chromium acetylacetonate electrolyte for redox flow batteries, Electrochem Commun. 12 (2010) 1634-1637.
8. R. Putt, Assessment of technical and economic feasibility of zinc/bromine batteries for utility load-levelling. EPRI report Em-1059, Project 635-1, Palo Alto, CA, Appendix M 1979.
9. K.J. Cathro, K. Cedzynska, D.C. Constable, Preparation and performance of plastic bonded carbon-bromine electrodes, J. Power Sources 19 (1987) 337-347.
10. M.J. Mader, R. White A Mathematical Model of a Zn / Br₂ Cell on Charge, J. Electrochem Soc. 133 (1986) 1297-1307.
11. I. Yamada, K. Miyazaki, T. Fukutsuka, Y. Iriyama, T. Abe, Z. Ogumi, Lithium-ion transfer at the interfaces between LiCoO₂ and LiMn₂O₄ thin film electrodes and organic electrolytes, J. Power Sources 294 (2015) 460–464.
12. H.S. Lim, A.M. Lackner, R.C. Knechtli, Zinc-Bromine Secondary Battery, J. Electrochem Soc. 124 (1977) 1154-1157.
13. P. Novak, K. Mueller, K.S.V. Santhanam, O. Haas, Conducting polymers for battery applications, Chem. Rev. 97 (1997) 207-282.
14. K.S.V. Santhanam, N. Gupta, Conducting polymer batteries: Present and future, Trends in Polymer Sci. 1 (1993) 284-286.
15. X. Dong, Y. Wang, Y. Xia, Re-building Daniell Cell with a Li-ion exchange Film, Scientific Reports 4, Article number 6916, 2014.

16. Z. Protich, K.S.V. Santhanam, A. Jaikumar, S. Kandlikar, P. Wong, Electrochemical Deposition of Copper in Graphene Quantum Dot Bath: Pool Boiling Enhancement, *J. Electrochem. Soc.* 163 (6) (2016) E166-E172.
17. C.A. Loto, I. Olefjord, H. Mattson, Electrodeposition of Zinc from Acid Based Solutions: A Review and Experimental Study, *Corros. Prev. Control J.* 39 (1991) 82-85.
18. J. Pushpavanam, Role of additives in bright zinc deposition from cyanide free alkaline baths, *Plat. Surf. Finish.* 73 (1986) 47-47.
19. M. Schlesinger, M. Paunovic, Electrodeposition of Zinc and Zinc Alloys in Modern Electroplating, 4th Edn., John Wiley and Sons, New York, pp: 423-46 (2000).
20. H.G. Todt, Studies on non-cyanide alkaline zinc electrolytes, *J. Solid State Electrochem.* 3 (1998) 48-51.
21. H.H. Geduld, Zincate or Alkaline Noncyanide Zinc Plating, ASM Intl., Metals Park, Ohio, pp: 90 (1998) 106.
22. M. Shanmugasigamani, J. Pushpavanam, J. Role of additives in bright zinc deposition from cyanide free alkaline baths, *Appl. Electrochem.* 36 (2006) 315-322.
23. M.C. Li, L.L. Jiang, W.Q. Zhang, Y.H. Qian, S.Z. Luo, J.N. Shen, Electrodeposition of nanocrystalline zinc from acidic sulfate solutions containing thiourea and benzalacetone as additives, *J. Solid State Electrochem.* 11 (2007) 549-553.
24. W.T. Zheng, Y.M. Ho, H.W. Tian, M. Wen, J.L. Qi, Y.A. Li, Field Emission from a Composite of Graphene Sheets and ZnO Nanowires, *J. Phys. Chem. C* 113 (2009) 9164-9168.
25. Y. Zhu, H.I. Elim, Y.L. Foo, T. Yu, Y. Liu, W. Ji, J.Y. Lee, Z. Shen, A.T. Wee, J.T. Thong, C.H. Sow, Multiwalled Carbon Nanotubes Beaded with ZnO Nanoparticles for Ultrafast Nonlinear Optical Switching, *Adv. Mater.* 18 (2006) 587-592.
26. J. Zeleny, The Electrical Discharge from Liquid Points, and a Hydrostatic Method of Measuring the Electric Intensity at Their Surfaces, *Phys. Rev.* 3 (1914) 69-91.
27. J. Wu, X. Shen, L. Jiang, K. Wang, K. Chen, A Solvothermal synthesis and characterization of sandwich-like graphene/ZnO nanocomposites, *Appl. Surf. Sci.* 256 (2010) 2826-2830.
28. K.S.V. Santhanam, S. Kandlikar, M. Valentina, Y. Yang, Electrochemical process for producing graphene, graphene oxide, metal composites, and coated substrates, US Patent 2016/0017502A1.
29. A. Jaikumar, K.S.V. Santhanam, S. Kandlikar, I.B.P. Raya, P. Raghupathi, Electrochemical Deposition of Copper on Graphene with High Heat Transfer Coefficient, *ECS Transactions* 66 (30)(2015) 55-64.

30. A.J. Bard, L.R. Faulkner, *Electrochemical Methods*, Wiley, NJ (2000).
31. A. Gomes, M.I. da Silva Pereira, Zn electrodeposition in the presence of surfactants: Part I. Voltammetric and structural studies, *Electrochim. Acta* 52 (2006) 863-871.
32. L.E. Moron, Y. Meas, R. Ortega-Borges, J.J. Perez-Bueno, H. Ruiz, G. Trejo, Effect of a poly(ethylene glycol) (MW 200)/benzylideneacetone Additive Mixture on Zn Electrodeposition in an Acid Chloride Bath, *Int. J. Electrochem. Sci.* 4 (2009) 1735-1753.
33. J.X. Yu, H.X. Yang, X.P. Ai, Y.Y. Chen, Effects of Anions on the Zinc Electrodeposition onto Glassy-Carbon Electrode, *Russian J. Electrochem.* 38 (2002) 321-325.
34. B.Z. Jugovi, T.L. Trišovi, J.S. Stevanovi, M.D. Maksimovi, B.N. Grgur, Comparative studies of chloride and chloride/citrate based electrolytes for zinc–polyaniline batteries, *Electrochim. Acta.* 51 (2006) 6268-6274.
35. J. McBreen, E. Gannon, Electrodeposition of Zinc on Glassy Carbon from ZnCl_2 and ZnBr_2 Electrolytes, *J. Electrochem. Soc.* 130 (1983) 1667-1670.
36. J.X. Yu, H.X. Yang, X.P. Ai, Y.Y. Chen, Effects of Anions on the Zinc Electrodeposition onto Glassy-Carbon Electrode, *Russian J. Electrochem.* 38 (2002) 321-325.
37. H. Fischer *Elektrolytische Absecheidung und Elektrokrystallisation der Metallen*, Springer, Berlin, 1954.
38. P.K. Leung, C. Ponce-de-Leon, C.T.J. Low, F.C. Walsh, Zinc deposition and dissolution in methanesulfonic acid onto a carbon composite electrode as the negative electrode reactions in a hybrid redox flow battery, *Electrochimica Acta.* 56 (2011) 6536–6546.
39. K. J. Cathro, Mass Transport during Zinc Electrowinning at High Current Density, *J. Electrochem. Soc.* 139(8) (1992) 2186-2192.
40. J.G. Albright, D.G. Miller, Mutual diffusion coefficients of aqueous ZnSO_4 at 25°C, *J. Sol. Chem.* 4(9) (1975) 809-816.
41. I. S. El-Hallag, Electrochemical studies and extraction of chemical and electrochemical parameters of Zn(II) ion at mercury Electrode via convolutive voltammetry and digital simulation methods, *J. Chil. Chem. Soc.* 55 (2010) 3.
42. E. Companys, M. Naval-sánchez, N. Martínez-micaelo, J. Puy, J. Galceran, Measurement of Free Zinc Concentration in Wine with AGNES, *J. Agric. Food Chem.* 56 (2008) 8296–8302.
43. J. Simonin, J.M. Ramos, J. Torres-Arenas, Diffusion coupling in multiply associating electrolyte solutions, *J. Molecular Liquids* 215 (2016) 69–76.

44. Z. Galus, Diffusion coefficients of metals in mercury, *Pure & Appl. Chem.* 56 (1984) 635-644.
45. X. Xio, A.J. Bard, Observing Single Nanoparticle Collisions at an Ultramicroelectrode by Electrocatalytic Amplification, *J. Am. Chem. Soc.* 129 (2007) 9610-9612.
46. Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon, J. Liu, Electrochemical Energy Storage for Green Grid, *Chem.Rev.* 111 (2011) 3577-3613..
47. Y.D. Chen, K.S.V. Santhanam, A.J. Bard, *J. Electrochem. Soc.* 129 (1982) 61-66.
48. S.J. Banik, R. Akolkar, Suppressing Dendrite Growth during Zinc Electrodeposition by PEG-200 Additive. *J.Electrochemical Soc.* 160 (2013) D519-D523.
49. B. R. Scharifker, G. Hills, Theoretical , experimental studies of multiple nucleation, *Electrochim. Acta.* 28 (1983) 879-889.
50. M. E. Hyde, R. G. Compton, Theoretical , experimental aspects of electrodeposition under hydrodynamic conditions, *J. Electroanal. Chem.* 549 (2003) 1-12
51. F. Peng, S.J. Qin, Y. Zhao, G.B. Pan, Zn Electrodeposition on Single-Crystal GaN(0001) Surface: Nucleation and Growth Mechanism, *International Journal of Electrochemistry*, ID3212703 (2016) 8 pages.
52. M. Roding, S. J. Bradley, M. Nyden, T. Nann, Fluorescence Lifetime Analysis of Graphene Quantum Dots, *J. Phys. Chem. C.* 118(51) (2014) 30282-30290.
53. X. Liu, W. Gao, X. Zhou, Y. Maa, Pristine graphene quantum dots for detection of copper ions, *J. Mater. Res.* 29 (2014) 1401-1407.
54. K. Habiba, V. I. Makarov, J. Avalos, M. J. F. Guinel, B. R. Weiner, G. Morell, Luminescent graphene quantum dots fabricated by pulsed laser synthesis, *Carbon*, 64 (2014) 341-350.
55. X. Fang, M. L. Kaimo Guo, J. Li, M. Pan, L. Bai, M. Luoshan, X. Zhao, Graphene quantum dots optimization of dye-sensitized solar cells, *Electrochimica Acta* 137 (2014) 634-638.
56. X. Shi, W. Gu, W. Peng, B. Li, N. Chen, K. Zhao, Y. Xian, Sensitive Pb²⁺ Probe Based on the Fluorescence Quenching by Graphene Oxide and Enhancement of the Leaching of Gold Nanoparticles, *ACS Applied Materials & Interfaces* 6 (2014) 2568-2575.
57. W. Yao, Y. Dai, K. Ge, J. Shi, J. Xu, Strongly coupled hybrid ZnCo₂O₄ quantum dots/reduced graphene oxide with high-performance lithium storage capability, *Electrochimica Acta* 210 (2016) 783-791.

58. S. Talam, S.R. Karumuri, N. Gunnam, Synthesis, Characterization, and Spectroscopic Properties of ZnO Nanoparticles, *ISRN NanoTechnology*, 2012 (2012), Article ID 372505
59. S.B. Rana, P. Singh, A.K. Sharma, A.W. Carbonar, R. Dogra, Synthesis and characterization of pure and doped ZnO nanoparticles, *J. Optoelectronics and Advanced Materials* 12 (2010) 257-261.
60. C. Ponce de Leon, A. Frias-Ferrer, J. Gonzalez-Garcia, D.A. Szanto, F.C. Walsh, Redox flow cells for energy conversion, *J. Power Sources* 160(2006) 716-732.
61. P.C. Li, C.C. Hu, H. Noda, H. Habazaki, Synthesis and characterization of carbon black/manganese oxide air cathodes for zinc–air batteries: Effects of the crystalline structure of manganese oxides, *J. Power Sources* 298 (2015) 102-113.
62. M. Sun, X. Yang, D. Huisin, R. Wang, Y. Wang, Consumer behavior and perspectives concerning spent household battery collection and recycling in China: a case study, *J. Clean. Prod.* 107 (2015) 775-785.
63. Y. Cheng, H. Zhang, Q. Lai, X. Li, Q. Zheng, X. Xi, C. Ding, Effect of temperature on the performances and in situ polarization analysis of zinc–nickel single flow batteries, *J. Power Sources* 249 (2014) 435-439.
64. K. Harting, U. Kunz, T. Turek, Zinc–air batteries: prospects and challenges for future improvement, *Z. Phys. Chem.* 226 (2012) 151-166.
65. Y. Li, H. Dai, Recent advances in zinc–air batteries, *Chem. Soc. Rev.* 43 (2014) 5257-5275.
66. C. Ponce de Leon, F.C. Walsh, Secondary Batteries – Zinc Systems | Zinc–Bromine Reference Module in Chemistry, Molecular Sciences and Chemical Engineering, from *Encyclopedia of Electrochemical Power Sources*, (2009) 487-496, Current as of 5 December 2015.
67. Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon, J. Liu, Electrochemical Energy Storage for Green Grid, *Chem. Rev.* 111 (2011) 3577–3613.
68. K. Ngamsai, A. Arpornwichean, Measuring the state of charge of the electrolyte solution in a vanadium redox flow battery using a four-pole cell device, *J. Power Sources* 298 (2015) 150-157.
69. Y.K. Zeng, T.S. Zhao, L. An, X.L. Zhou, L. We, A comparative study of all-vanadium and iron-chromium redox flow batteries for large-scale energy storage, *J. Power Sources* 300 (2015) 438-443.

70. H. Sun Yang, J. Ho Park, H. W. R, C.S. Jin, J.H. Yang, Critical rate of electrolyte circulation for preventing zinc dendrite formation in a zinc-bromine redox flow battery, *J. Power Sources* 325 (2016) 446-452.
71. D. Ma, H. Wang, Y. Li, D. Xu, S. Yuan, X. Huang, X. Zhang, Y. Zhang, *In situ* generated FeF_3 in homogeneous iron matrix toward high-performance cathode material for sodium-ion batteries, *Nano Energy* 10 (2014) 295-296.
72. X. Huang, R. Wang, D. Xu, Z. Wang, H. Wang, J. Xu, Z. Wu, Q. Liu, Y. Zhang, X. Zhang, Homogeneous CoO on Graphene for Binder-Free and Ultralong-Life Lithium Ion Batteries, *Adv. Funct. Mater.* 23 (2013) 4345-4346.
73. D. Ma, Z. Cao, H. Wang, X. Huang, L. Wang and X. Zhang, Three-dimensionally ordered macroporous FeF_3 and its *in situ* homogenous polymerization coating for high energy and power density lithium ion batteries, *Energy Environ. Sci.* 5 (2012) 8538-8542
74. J. Cheng , L. Zhang , Y. S. Yang , Y. Wen, G. Cao, X.D. Wang, Preliminary study of single flow zinc–nickel battery, *Electrochemistry Communications* 9 (2007) 2639-2642.