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Hybrid Electrochemical Behaviour of La_{1-x}CaxMnO₃ Nano Perovskites and Recycled Polar Interspersed Graphene for Metal-Air Battery System

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Accumulations of waste dry cell batteries create irreparable damage to the environment. To address this issue, herewith we recycle the graphite electrode from waste dry cells to serve as a precursor for synthesising graphene electrolyte additives in metal-O₂ battery system. Magnesium-O₂ battery is an interesting option due to its high theoretical energy density (6800 WhKg⁻¹) but tuning the electrode-electrolyte interfacial layer plays a major role. Utilizing La_{1-x}CaxMnO₃ (x = 0.70, 0.80 and 0.90) manganite perovskite and polar interspersed graphene as protective electrode-electrolyte passivation layers, drastically increases the battery performance. La_{1-x}CaxMnO₃ protective layer enhances the charge separation, charge transfer, reaction kinetics and reduces the charge recombination at the electrode surface. The specific discharge capacity of newly prepared La_{1-x}CaxMnO₃/interspersed graphene based Mg-air battery system is 1595.3 mAhg⁻¹, which makes it more superior to regular Mg-O₂ battery (890 mAhg⁻¹). The interspersed graphene -based Mg/La_{1-x}CaxMnO₃ air battery shows excellent discharge capacity and notable electrochemical characteristics, which opens whole new spectrum of opportunity in modern electric vehicles.

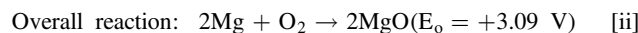
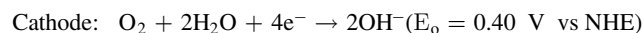
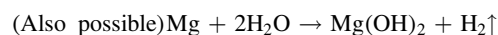
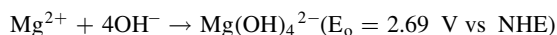
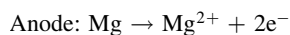
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Energy storage devices play a vital role in present and future electrochemical technologies.^{1,2} Batteries are one of the most crucial energy storage devices that make fascinating application in movable electronics and electric vehicles. Batteries are well-known for its relatively high energy density, stable discharge voltage and electronic ability.^{3,4} Metal-air batteries have immense potential to charge flexibility and static applications.⁵ Metal-O₂ batteries possess low construction price which make them attractive.⁶ Air breathable cathode and a metal anode along with relevant electrolyte decorate the metal-air battery system. Open cell configuration of metal-air batteries makes it convenient and also allows O₂ to be used directly from air without pre incorporation. This open cell configuration leads to their high theoretical energy densities.⁷ Moreover, charging time of a metal air battery can be minimized through mechanically recharging of metal anode.^{8,9} Metal-O₂ batteries are classified in to different types like Li-O₂ and Zn-O₂ batteries,^{10,11} which are popularly used; conversely Mg-O₂ batteries are comparatively less explored. Mg-O₂ batteries are renowned for its sustained discharge time, reduced cost, tremendous theoretical output voltage (3.09 V), elevated theoretical energy density (6800 WhKg⁻¹), lesser weight, recyclability and eco-friendly aspect.^{12,13} The open circuit voltages of sea-urchin type nanostructure based Mg anode is 1.42 V and that of two spheres nanostructure is 1.32 V.¹⁴ Concurrently the discharge of Mg-O₂ battery, involves dissolution of Mg anode to deliver Mg²⁺ ions making two electrons,



The above reaction offers a standard electrode potential of 2.37 V and a discharge capacity of 2.2 Ahg⁻¹. As Mg-O₂ cells are concern, the redox reaction accompanies transfer of hydroxyl ion from air cathode to Mg anode. On the whole, electrochemical reactions of magnesium anode and O₂ cathode that occurs during the discharge studies can be elucidated by the following reactions,



In general, the experimental energy density of Mg-air battery is lower than theoretical one (6800 Whkg⁻¹)¹⁵ owing to the reasons like low performance of electrodes that suffers from corrosion, poor mechanics in formation of electrode passivation layers and prolonged dynamics of the oxygen reduction reaction (ORR) occurring at air cathode. Like-wise, hydrogen evolution reaction (HER) rendering hydrogen gas on the surface of Mg anode diminishes the performance of air battery, reduces the efficiency of working electrodes, lowers the battery life and eats up the electrolyte generating *negative difference effect*.^{16,17} Major pull back of the air battery is because of this negative difference effect and less electrode-electrolyte efficient usage. Further, galvanic corrosion plays a significant role when Mg anode of optimum reduction potential (2.37 V) readily comes in contact with secondary metals beneath its reduction potential. Possibilities of reducing corrosion impacts in metal air batteries hold the inclusion of cadmium (Cd), lead (Pb), mercury (Hg). Nonetheless, these metals possess heavy toxicity and cause dreadful environmental consequences.¹⁸ Organic surfactants can be used in Mg-air battery to improve the efficiency of electrodes sluggish operations. However, wobbly adsorption process of surfactants restrains this concept.¹⁹ One efficient way to improve battery performance, life time, and electrode dynamics, conceal anodic corrosion is to do surface coating of electrodes with other metallic oxides. Combination of different metal oxide coatings can be more beneficial. Alternatively, perovskite oxide material coatings can be effectively used to improve the predominant characteristics of air battery. Along with electrode coatings, catalysts and additives in electrolyte can boost up the battery performance.

The development of perovskite materials has been extensively explored in the different sectors of telecommunication, information technology, health care and electronics.²⁰ Enchanting characteristics of perovskite materials can be modified through superconductivity, colossal magnetoresistance (CMR) properties. Lanthanum manganite (LaMnO₃) and calcium intercalated lanthanum manganite belong to ABO₃ perovskite oxide family.²¹ Lanthanum being a rare earth ion adopts twelve co-ordinates of A-sites and manganese as a well-known transition metal take up the octahedral B-sites forming LaMnO₃. Electrical conductivity and catalytic action of

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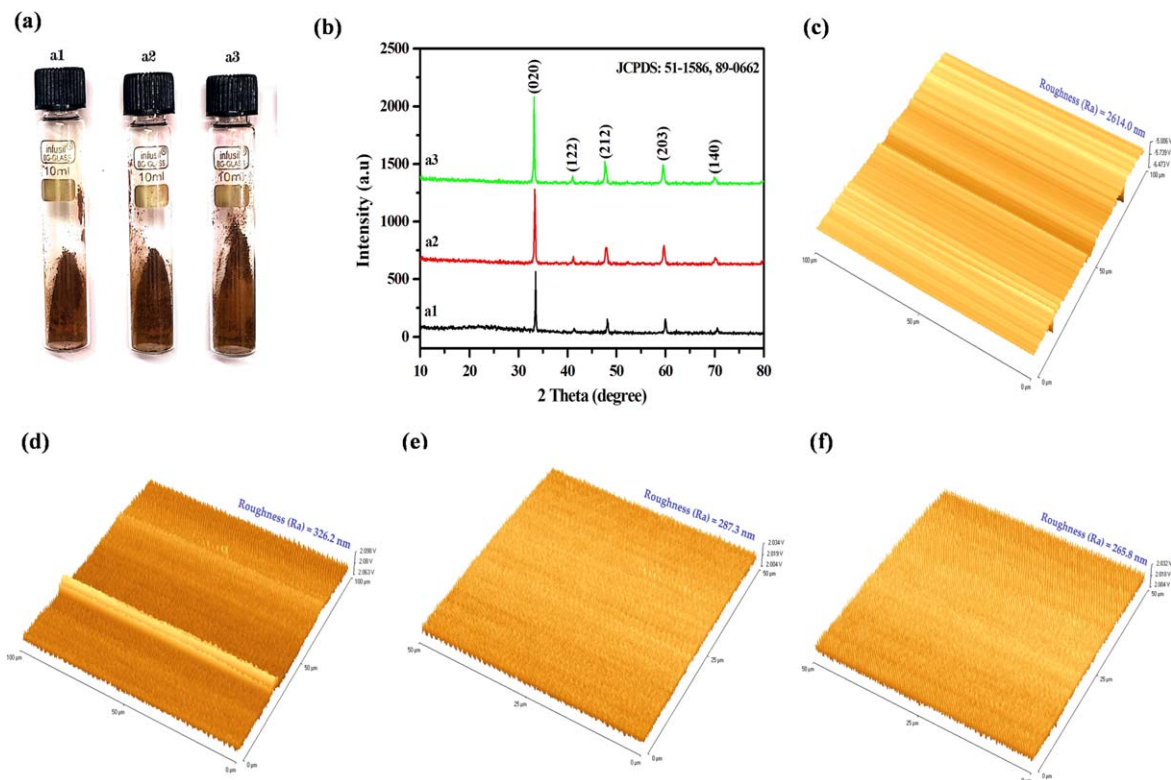


Figure 1 (a) Images of prepared perovskite samples. (b) XRD spectrum of a1, a2 and a3 perovskite nanoparticles. (c) AFM image of bare Mg electrode surface. (d) AFM image of Mg/a1 electrode surface. (e) AFM image of Mg/a2 electrode surface. (f) AFM image of Mg/a3 electrode surface.

LaMnO_3 are triggered undoubtedly while La is replaced moderately with calcium (Ca). This is because structure of the perovskite gets well-stacked in correspondence to increase in size of cations at A-sites.²¹ Further calcium doped lanthanum is more attractive and has been widely used in fuel cells, corrosion resistance, electrode material and thin film sensor.²² $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ has an admirable thermal expansion identical with Ytria Stabilized Zirconia (YSZ) electrolytes.²³ $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ is a conductive material that has shown high electronic stability.²⁴ The general form of rare earth doped mixed valent perovskite manganite materials especially La based is $\text{La}_{1-x}\text{A}_x\text{MnO}_3$, where A is the divalent earth ion like strontium, calcium, lead and iron. In this study, the incorporation of non-stoichiometric ratios of calcium to be the major composition as calcium has lesser atomic radius and high stability when compared with La and Mn. By substituting Ca for La, an awe-inspiring mixed valent perovskite with partial insulating behaviour will be formed.

In just a short-while, carbon nanomaterials picked up the market through its excellent catalytic performance in energy storage devices.^{25,26} Accumulation of sectional passivation oxide layers on electrode originated from electrolytic salt reaction that will improve the battery performance by suppressing the anodic corrosive breakdown.²⁷ Graphene is one atomic thick layer of carbon atom acquiring hexagonal mesh structure with honey comb framework²⁸ holding admirable conductivity and anti-corrosive stability.²⁹ Owing to its inertness, giant temperature stability and high discharge capacity (610 mAhg^{-1}), graphene based materials are preferably used in electronics.³⁰ Graphene's appreciable catalytic action and gas adsorbent property makes it to be an active catalyst supporting electrochemical redox reactions.³¹ Low dimensional graphene exhibit huge surface area, contributing to improvement in surface active sites, electrical conductivity, thermal sustainability.³² Modernistic strategy for graphene production were intensified nowadays adopting nano-mechanical exfoliation, peel-off scotch tape technique, vapour deposition methods, epitaxial growth, unwinding of carbon tubes and by organic approach.³³ Choice for synthesis of graphene is still confronting and being enrooted. In account of

endowing higher yield rates, colloidal hummer's method in association with tenacious oxidizing promoter serves to be the finest approach. Typical production of polar interspersed graphene (IG) by chemical synthesis (Hummer' method) needs graphite to be used as a precursor material which involves more cost. Instead, to curtail the cost, as well as to reduce the waste deposits of battery, an inherently planned method of utilizing disposed Zn-C battery electrodes as graphite precursor is experimented in this work.

In this regard, a first novel attempt was made to incorporate the upgraded perovskite particles of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.70, 0.80, 0.90$) as thin film coating on Mg electrode through doctor blade technology.^{34,35} The performance of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.70, 0.80, 0.90$) thin film coated Mg anode in 6 M KOH and polar interspersed graphene (IG) based 6 M KOH electrolytes is examined by studying their discharge and electrochemical characteristics. Moreover to figure out the repercussion of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ coated electrode, we performed standard electrochemical impedance spectroscopic studies, tafel polarisation studies and oxidation-reduction kinetic studies using cyclic voltammetry. In order to firmly study the electrode surface attributes during pre and post polarisation studies, scanning electron microscopy was used. Graphene was not preferably used as electrode coating as it exposes a sturdy energy barrier, creating absolute restriction of oxygen diffusion in to the electrode.³⁶ This leads to weaker bonding of O_2 on to the bald surface of graphene effecting the diminishment of active reaction sites and easier jump of oxygen atoms to lower free vacancy co-ordination sites at edge boundaries. As the result, oxygen atom losses its energy and minimizes the oxidation barrier making pure graphene electrode coatings as slack-spined.

Experimental

Sample preparation.— $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ nano-perovskite ceramic samples with distinctive proportions of x , ($x = 0.70, 0.80$ and 0.90), hereafter named as a1, a2 and a3 respectively were synthesised using an ultra-sonochemical reactor employing solid state technique.³⁷

Authentic analytical pure grades of lanthanum nitrate $\text{La}(\text{NO}_3)_3$ (99.9% Merck, USA), manganese carbonate $\text{Mn}_2(\text{CO}_3)_3$ (99.9% Sigma-Aldrich, USA) and calcium nitrate (99% Himedia, India) powders in stoichiometric ratios were weighed in a digitalized balance and blended using a silica-agate mortar. The similar procedure was adapted to synthesis the a1, a2 and a3 perovskite. Samples were then transferred to a muffle furnace for immediate calcination at 973 K for 8 h and repeatedly grinded to procure a homogeneous mixture. The obtained nano perovskite was squashed and moulded in to circular pellets employing hydraulic pellet maker (KIMAYA, India) for further characterization studies. Equal quantities (0.3 g) each of a1, a2 and a3 were taken. A cleaned Mg strip of length 6 cm, breadth 0.3 mm and thickness 0.02 mm was polished with sheets of SiC grid followed by acetone wash. Slurry was prepared taking up, 0.3 g of the perovskite well-mixed with polyvinylidene fluoride ($\text{C}_2\text{H}_2\text{F}_2$)_n binder pursued by drop casting of N-Methyl-2-pyrrolidone ($\text{C}_5\text{H}_9\text{N}$) with the weight ratio of 8:1.5:0.5. The prepared slurry was coated on the negative electrode by doctor blade technique.³⁷ The thickness of the coating is estimated to be 1.2 μm using digital screw gauge.

Excess e-waste and battery waste was procured by Arrkay Engineering Works, near Ekkatuthangal, Guindy, India. On inspecting this issue, we flourished an idea of reusing the waste dry cell electrodes, to remanufacture graphite powders. After procuring mutual congruence from Arrkay Engg Works, we collected the waste dry cells free of cost from the Guindy estate-area. At first, broken and flawed battery cells were discarded safely. Then, furnished battery cells were opened up by twining the outer sealed tin-metal covers using cylindrical saw blade and twisters. The plastic housing layers were removed by scarping and consequently electrode was removed from the cell. To get rid of impurities like MnO_2 , carbon-metal fragments, the electrode was scrubbed, soaked in water and dried for discrete number of times. Later, the electrodes were crumbled and squashed to yield exquisite graphite powders. The obtained graphite powder was treated with hydrochloric acid and nitric acid accompanied by multiple times centrifuging to further eradicate the organic chemical impurities.

Finally, re-produced graphite powders were heated at 70 °C for a day. To synthesise polar interspersed graphene, analytical grades of chemicals (Merck, Himedia, and Sigma Aldrich; 99%) were used without any further purification employing Hummers method.³⁸ To disentangle flakes of graphite, an active ultra-sonication setup for 5 h was performed by adding 3 g of reproduced graphite oxide, 1.5 g of sodium nitrate (NaNO_3) in 150 ml of concentrated sulphuric acid (H_2SO_4). Later, beneath intense stirring and at 30 °C, 12 g of potassium permanganate (KMnO_4) was added bit by bit for nearly 6 h. Instantly, the colour of the solution changes from pink to dark brown. With continuous stirring for 2 days, 250 ml of deionized water was added tenderly in to the mixture. Further at 70 °C, 200 ml of deionized water was added to the system to clear away unused KMnO_4 . The obtained system of solution was then dried at 80 °C forming graphene oxide nanoparticles. 2 g of as-prepared graphene oxide was mixed with 100 ml of water, followed by slow addition of 5 ml hydrazine hydrate (H_2O_2) kept under reflux-stirring at 80 °C for 12 h and then dried at 393 K. Observable colour change from dark brown to light yellowish brown exists indicating the reduction mechanism of graphene oxide to reduced graphene. Suspension of 0.5 g graphene in 100 ml of deionized water was kept in ultra-sonication followed by gradual addition of 1 g sodium hydroxide dissolved in 50 ml of deionized water to accomplish ultimate pH of 7.5–8. At last, the prepared solution was centrifuged dried at 80 °C for 24 h to obtain polar IG. The prepared samples of a1, a2, a3 were shown in Fig. 1a. Here, interspersed graphene signifies the graphene particles that are capable of forming suspended homogeneous electrolyte solution.

Material characterization.—X-ray diffraction analysis was availed for examining the crystalline nature of a1, a2, a3 and IG through X'Pert Pro, Pan-Analytical diffractometer using $\text{CuK}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation source running at 40 kV and 20 mA current rate. Scan range (2θ) was from 10° to 80° at room temperature (298 K). Scanning electron microscopy coupled with energy dispersive spectrometer (SEM-EDX; JEOL JSM-6390LV) operating at 20 kV was used to study the surface characteristics of prepared samples. Atomic force microscopy (AFM; SPM Innova, version 6; Veecodi,

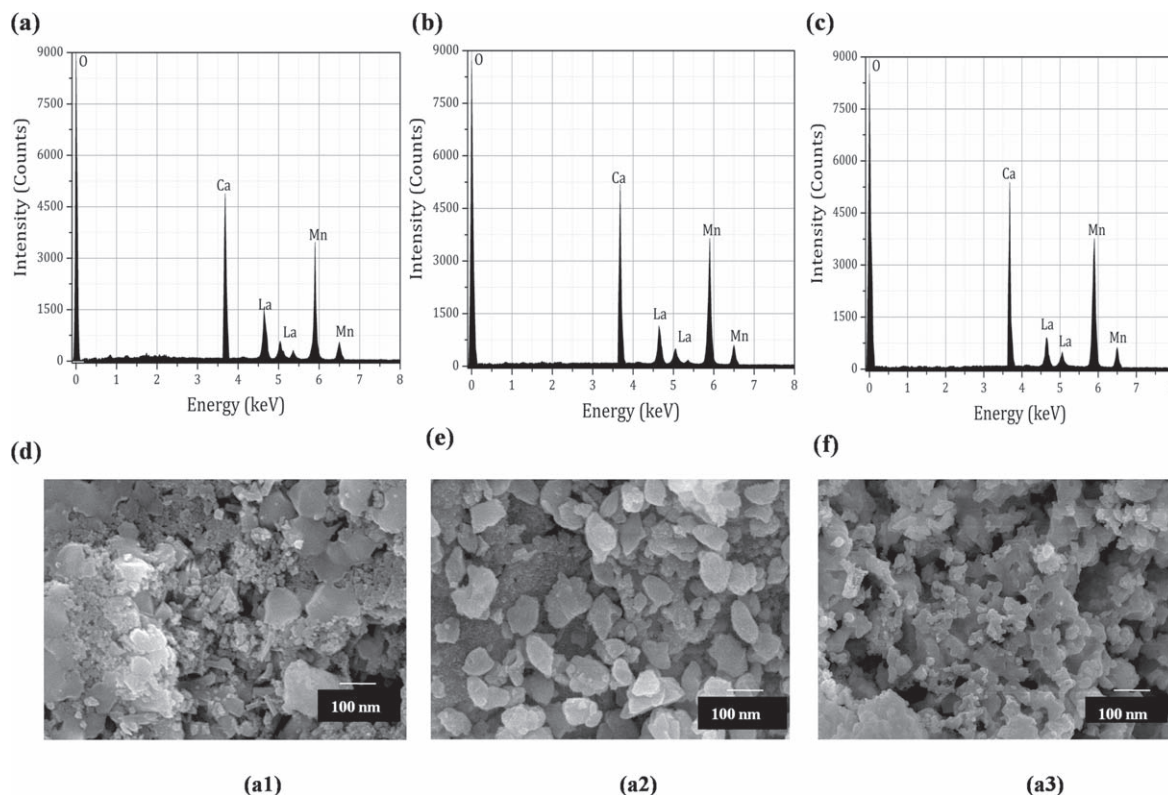


Figure 2 (a) EDX spectrum of a1 perovskite sample. (b) EDX spectrum of a2 perovskite sample. (c) EDX spectrum of a3 perovskite sample. (d) SEM image of a1 sample. (e) SEM image of a2 sample. (f) SEM image of a3 sample.

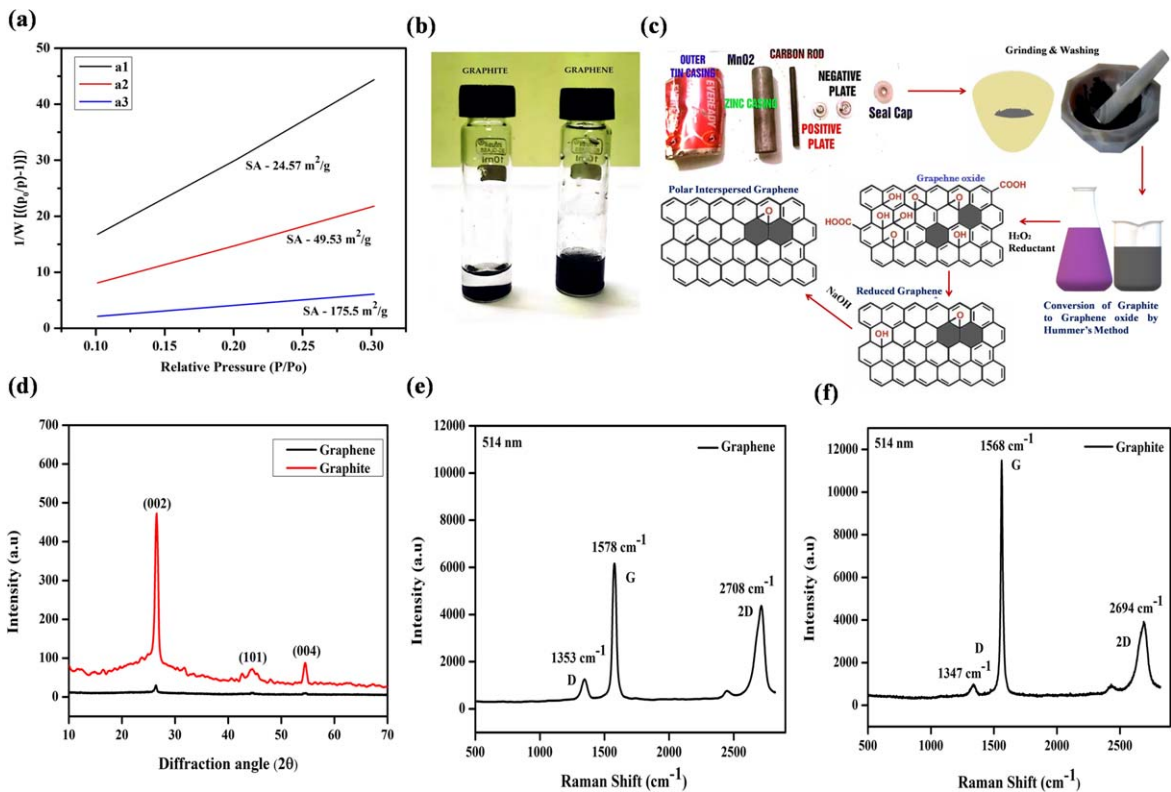


Figure 3 (a) Surface area measurement (b) Images of prepared interspersed graphene (c) Schematic illustration of polar interspersed graphene preparation. (d) XRD spectrum of graphite and graphene nanoparticles. (e) Raman spectrum of graphite. (f) Raman spectrum of graphene.

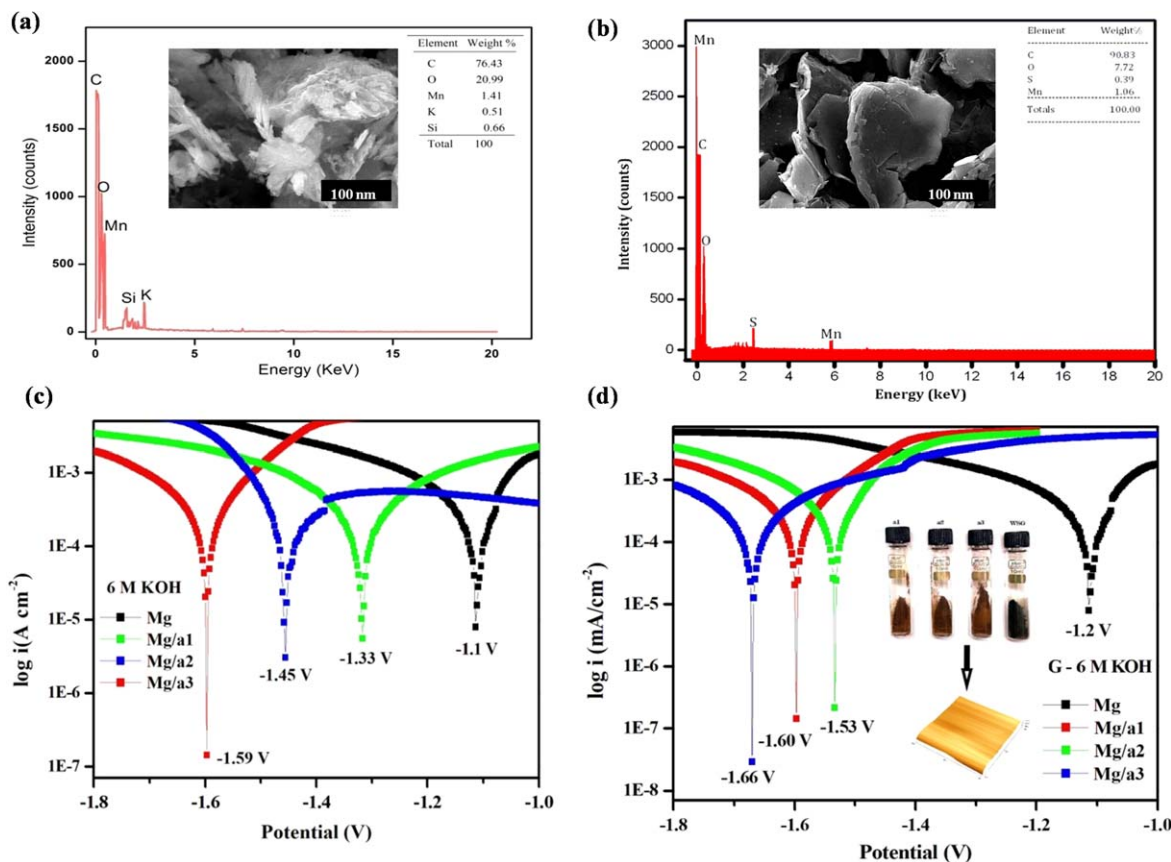
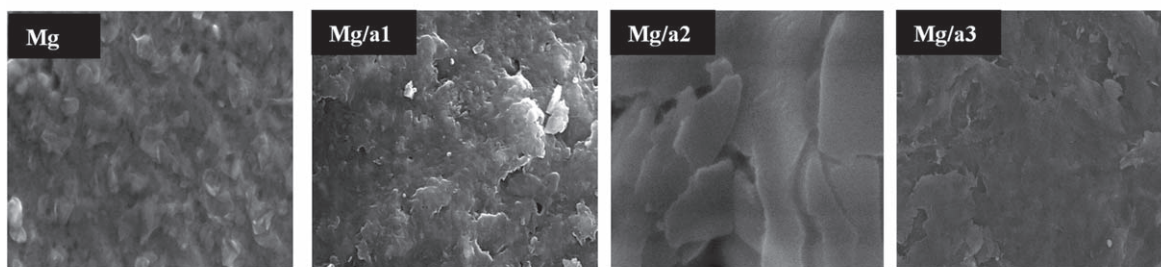


Figure 4 (a) EDX spectra and SEM image of graphite. (b) EDX spectra and SEM image of graphene. (c) Tafel polarisation plots for Mg, Mg/a1, Mg/a2, Mg/a3 electrodes in 6 M KOH. (d) Tafel polarisation plots for Mg, Mg/a1, Mg/a2, Mg/a3 electrodes in IG-6M KOH.

6M KOH



IG- 6 M KOH

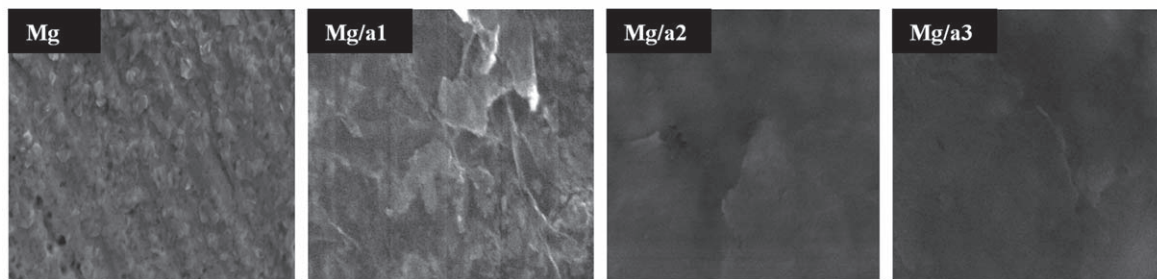


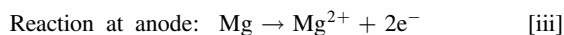
Figure 5 SEM image of Mg, Mg/a1, Mg/a2, Mg/a3 electrodes in 6 M KOH and IG-6M KOH.

Table I. Corrosion parameters obtained from tafel polarisation studies.

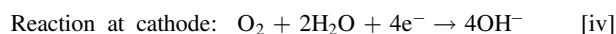
(a) Corrosion Parameters				
Electrolyte	Sample	Corrosion Potential (vs SCR. E.) V^{-1}	Corrosion Current Density ($mAcm^{-2}$)	C rate (mm/year)
6 M KOH	Mg	−1.10	5.62	1.95
	Mg/a1	−1.33	4.87	1.15
	Mg/a2	−1.45	3.75	0.97
	Mg/a3	−1.59	3.41	0.82
IG – 6M KOH	Mg	−1.20	5.54	1.17
	Mg/a1	−1.53	3.53	0.85
	Mg/a2	−1.60	3.26	0.06
	Mg/a3	−1.66	3.04	0.02

USA; Sb-Si probe) employed under contact mode with the scan range area of 50–60 μm and scan rate of 30 μms^{-1} was used to explore the surface roughness of perovskite (a1, a2, a3) coated anode. Raman spectra (WI Tech alpha, Japan) using Nd:YAG source was used for the vibrational mode analysis.

Mg-O₂ battery construction.—Mg-strip of $6 \times 0.3 \times 0.02$ cm dimension was used as anode and processed for coating. Perovskite (a1, a2 and a3) coated Mg anode, serves as negative electrode hereafter named as Mg/a1, Mg/a2 and Mg/a3 respectively. At the anode, Mg oxidizes to form Mg^{2+} and two electrons.

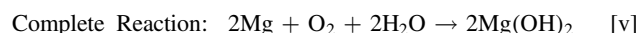


Individual air cathodes with the lofty sharp flow of O₂ designed using inert stainless steel (SS) mesh of pore size ~ 1 mm was used. Mesh of SS delivers an efficacious role by varying the oxidation-reduction reaction kinetics through regulation of O₂ flow.³⁹ The mesh was wrapped around the inner circumference of the beaker. At the cathode, air combines with water and reduces to hydroxyl ion.



This supreme SS meshed air cathode with flamboyant perovskite coated Mg-anode immersed in 200 ml of 6 M KOH and 200 ml of (0.2 g) IG-sprinkled 6 M KOH electrolytic bath solutions constitutes

the construction of two distinct Mg-O₂ battery. Further, IG added 6 M KOH electrolyte and bare 6 M KOH solution were sonicated at 50 KHz frequency for 10 min to obtain a homogeneous solution. Roughly 5.5 cm of the perovskite coated Mg-strip (anode) was dipped in to the electrolytic solution contributing the effective surface area of 3.53 cm². The over-all electrochemical reaction behind the Mg-O₂ battery is as follows,



Electrochemical measurements.—Electrochemical measurements were performed using well-equipped electrochemical workstation (PGSTAT302-N; MetrohmAutolab, Netherlands). The corrosive nature analysis of Mg/a1, Mg/a2 and Mg/a3 samples was demonstrated with the potential window ranging from −1.0 to −1.8 V using a three-electrode cell configuration. Platinum was used as the counter electrode and saturated calomel electrode (SCE) was used as the reference electrode (0.241 V vs SHE) with potential referencing to SCE. Tafel polarisation measurements were explored in both 6 M KOH and IG-6M KOH electrolytes for individually coated Mg/a1, Mg/a2 and Mg/a3 electrodes. Extrapolated tafel slope was acquired for the I_{corr} rate and negative potential window at the scan rate of 3 mVs^{−1}. Applying the procured polarisation resistance (R_p) and extrapolated tafel slopes, the corrosion density i_{corr} and rate of corrosion C_r was calculated by the formula,

Table II. Weight loss data of a1, a2 and a3 coated Mg anode in 6M KOH and IG-6M KOH.

Conditions	Weight (W) loss of a1, a2, a3 (g) coated on Mg anode in 6M KOH electrolyte						Weight (W) loss of a1, a2, a3 (g) coated on Mg anode In IG-6M KOH electrolyte					
	1.20 g	—	1.19g	—	1.21g	—	1.20 g	—	1.20 g	—	1.21 g	—
a1		W loss	a2	W loss	a3	W loss	a1	W loss	a2	W loss	a3	W loss
Before coating on Mg strip)	1.50 g	0.0 g	1.49 g	0.0g	1.51 g	0.0g	1.5 g	0.0 g	1.5 g	0.0 g	1.51 g	0.0 g
After coating left for 1 h	1.49 g	0.01 g	1.48 g	0.01g	1.50 g	0.01g	1.49 g	0.01 g	1.49 g	0.009g	1.50 g	0.007g
After coating left for 2 h	1.46 g	0.03g	1.46 g	0.02g	1.49 g	0.01g	1.47 g	0.02 g	1.48 g	0.01 g	1.49 g	0.01 g
After coating left for 3 h	1.43 g	0.03g	1.44 g	0.02g	1.46 g	0.03g	1.43 g	0.04 g	1.45 g	0.03 g	1.47 g	0.02 g
After coating left for 4 h	1.39 g	0.04g	1.39 g	0.05g	1.42 g	0.04g	1.38 g	0.05 g	1.41 g	0.04 g	1.43 g	0.04 g
After coating left for 5 h	1.31 g	0.08g	1.32 g	0.07g	1.36 g	0.06g	1.32 g	0.06 g	1.34 g	0.07 g	1.34 g	0.07 g
After coating left for 6 h	1.21 g	0.10g	1.21 g	0.11g	1.23 g	0.13g	1.24 g	0.08 g	1.25 g	0.09 g	1.27 g	0.08 g
a1–0.29 g			a2–0.28 g		a3–0.28 g		a1–0.26 g		a2–0.25 g		a3–0.24 g	

Table III. Impedance parameters obtained from nyquist plot.

6M KOH electrolyte			IG- 6M KOH		% Efficiency	
Specimen	Solution Resistance (R_s) (Ω)	Charge Transfer Resistance (R_{ct}) (Ω)	Solution Resistance (R_s) (Ω)	Charge Transfer Resistance (R_{ct}) (Ω)	(R_s) %	(R_{ct}) %
Mg/a1	6.4	28.5	9.98	47.9	55.93	68.07
Mg/a2	10.3	31.6	16.2	53.6	57.28	69.62
Mg/a3	12.7	34.2	20.1	59.8	58.26	74.85

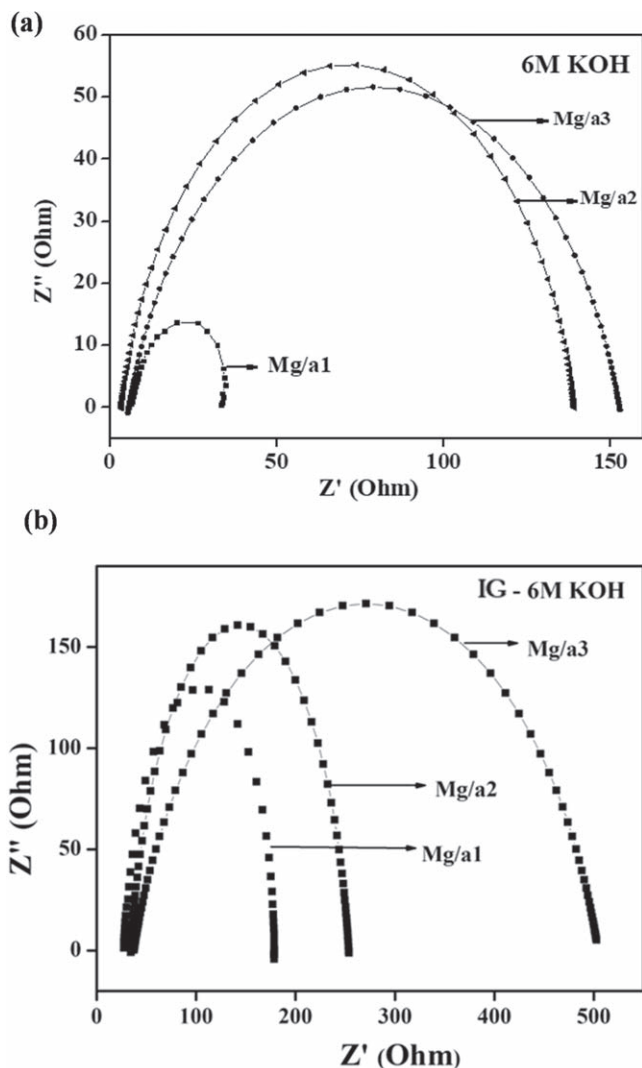


Figure 6 (a) Nyquist plot of Mg/a1, Mg/a2, Mg/a3 electrodes in 6 M KOH. (b) Nyquist plot of Mg/a1, Mg/a2, Mg/a3 electrodes in IG-6 M KOH.

$$i_{\text{corr}} = \frac{\beta_a^* \beta_c}{2.303 R_p^* (\beta_a + \beta_c)} \quad [\text{vi}]$$

$$C_{\text{rate}} = \frac{(3272 \cdot i_{\text{corr}} \cdot W)}{\rho} \quad [\text{vii}]$$

Where β_a and β_c are anodic and cathodic tafel constants. W is the equivalent weight in grams, 3272 is a conversion factor to mm/year. Electrochemical impedance measurements performed using electrochemical impedance spectroscopy (EIS). Mg/a1, Mg/a2 and Mg/a3 samples in both 6 M KOH and IG-6 M KOH was analysed using three-cell electrode set-up with the frequency range of 100 KHz to 1 MHz at the AC impedance of 6 mV. Discharge studies were performed on 6 M KOH and IG-6 M KOH electrolytes at constant current discharge of 20 mA (i.e., current density of 5.66 mAcm^{-2}). The plot between current density and life time was observed up to 0.3 V accounting for the discharge characteristics. Short-circuit studies were performed in both the electrolytes with legitimate time interval of 5 min for 30 min discharge cycle. Cyclic voltammetry studies for Mg/a1, Mg/a2, Mg/a3 in KOH and IG-KOH was performed using three cell electrodes as in tafel-polarisation studies at scan rate of 100 mV s^{-1} .

Adhesion test.—A simple scotch tape adhesion test was used to investigate the effectiveness of coating on the electrode surfaces

before and after tafel polarisation studies in both the electrolytes. At room temperature, a pressure sensitive single side adhesive tape was used. To increase the adhesion, the tape was glazed enduringly over the Mg electrode and substantially peeled by applying force on the opposite direction at 90° .⁴⁰ For conformation, the test was repeated thrice. Like-wise weight loss studies for the electrodes in both the electrolytes with the duration of 6 h accompanied by the time interval of 1 h was done. Here, an elementary impressive technique of just immersing the electrodes in both the electrolytes and measuring their weight loss with respect to time by digital balance was carried out.

Results and Discussion

$\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$.—XRD pattern of the a1, a2 and a3 perovskite samples were displayed in Fig. 1b affirming the presence of orthorhombic $pnma$ space group with lattice parameters $a = 0.5469 \text{ nm}$, $b = 0.5452 \text{ nm}$ and $c = 0.7712 \text{ nm}$ in near accord to JCPDS 51-1586 and 89-0662.⁴¹ While inspecting the Wyck off space group positions, using International Tables for Crystallography,⁴² it was founded that the single $pnma$ unit cell has 20 atoms and atoms gets stacked in Y direction upon increasing the divalent (Ca^{2+}) ion content. It is significant from the XRD pattern that on increasing the divalent ion concentration, there exists a shifting of peaks towards higher diffraction angle. In this regard, the 2θ values for highly raised peaks are 33.2586, 33.3684 and 33.4186 for a1, a2 and a3 respectively. By using scherrer formula, average crystallite size of a1, a2 and a3 samples were calculated as 49, 31, 22 nm in reference to the measurement of full width half maximum (FWHM) of the diffracted peaks. It's apparent that concentration of divalent ion increases in correspondence to decrease in crystallite size. Also a notable decrease in magnitude and increase in peak broadening for the entire plane was observed while increasing the divalent ion concentration Fig. 1b. This may be justified as the divalent ion substitution (Ca^{2+}) for element La will exhibit significant changes in single valent Mn to mixed valent i.e., trivalent and tetravalent, thereby intensifying oxidation reactions and reducing DE spin-spin interactions between Mn^{3+} and Mn^{4+} via oxygen orbital. Also the oxygen hopping mechanism while heating may lead to different functionalities and structural changes. AFM image in Figs. 1c–1f depicts the surface topography of Mg electrode, and a1, a2, a3 coated Mg electrodes respectively. The surface roughness (R_s) was 2614 nm for bare Mg electrode and 326.2 nm, 287.3 nm and 265.8 nm for a1, a2 and a3 coated electrode. It's observable that surface roughness of bare Mg is higher than coated electrodes may be because of uneven protrusions in the Mg strip. Whereas, coated samples encounter slight variations in their surface roughness. Figure 2. shows the EDX pattern and SEM images of a1, a2 and a3 nano-perovskites confirms the steady increase in Ca content while deteriorating La concentration up to certain extent. The compositional values in atomic % were shown in Fig. 2., that well-matched with the atomic composition of initiated precursors. Further SEM images confess patched frame-work like cage morphology with adherence of agglomerated particles in boundary phases. On close observation, minuscule pores over the vast surface of samples can be seen, which may be due to the liberation of substantial amounts of O_2 during heat exhaust and sonication. Thus, uneven grain boundaries and one to one clutched particles, makes it challenging to calculating the particle size. The surface area profile is shown in Fig. 3a. Implies that a3 has very large ($175.5 \text{ m}^2\text{g}^{-1}$) surface area compared to a2 ($49.53 \text{ m}^2\text{g}^{-1}$) and a1 ($24.57 \text{ m}^2\text{g}^{-1}$) perovskite samples. This observed large surface area for a3 is due to the lesser particle size possessed by a3.

Graphene.—The synthesised IG nanoparticles and procedure for synthesis is shown in Figs. 3b, 3c. Figure 3d shows the XRD pattern for graphite (precursor from waste dry cell) and graphene. The acute peak at 26.32° (002), expanded peak at 43.68° and 56.40° (004) confirms the presence of graphite. Characteristic peak for graphene

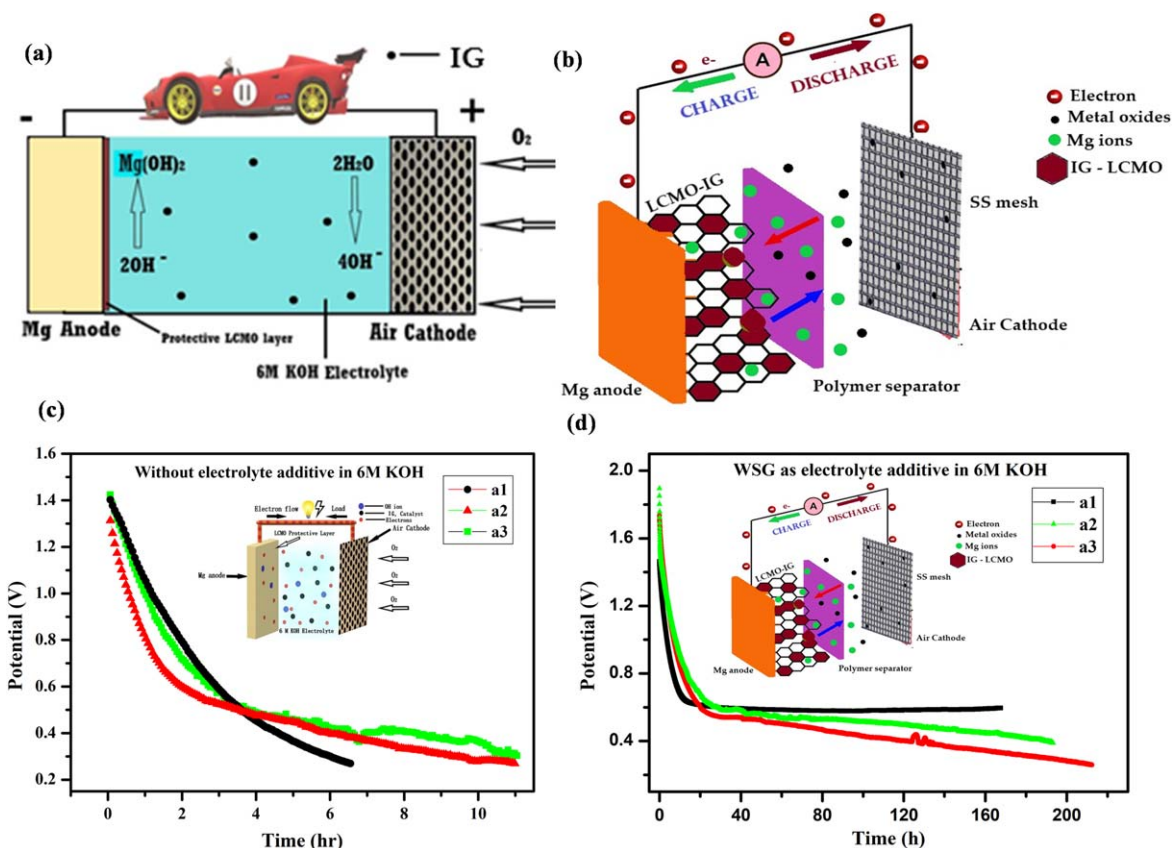
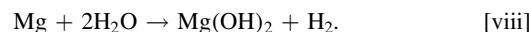


Figure 7 (a) Schematic representation of Mg-air battery with redox reactions. (b) Working of Mg/LCMO air battery. (c) Construction and mechanism of Mg/LCMO air battery. (d) Discharge studies of Mg/a1, Mg/a2 and Mg/a3 electrodes in 6 M KOH. (e) Discharge studies of Mg/a1, Mg/a2 and Mg/a3 electrodes in IG-6M KOH.

was most prominent at 26.50° (002) in accordance to hexagonal crystal lattice with $p63/mmc$ space group (JCPDS 411487). Peaks at 43.0° and 56.0° vanishes in graphene may be because of the appreciable reduction of oxygen functionalities, 1-D stacking with desirable hybridization (Sp^2).⁴³ Raman spectrum in Fig. 3e shows the first order G band at 1568 cm^{-1} with predominant intensity at E_{2g} mode and high order double resonance 2D band at 2694 cm^{-1} for graphite. Figure 3f shows the Raman spectrum of graphene with G band at 1578 cm^{-1} , D band at 1353 cm^{-1} and 2D band at 2708 cm^{-1} confirming the presence of graphene. The intensity of bands in graphite seems to be higher than graphene, due to resonance enhancement (G) and double resonance enhancement effects (2D). Easily notable high disorder induced D bands are approximately near 1351 cm^{-1} in both graphene and graphite and this disorder is because of in-plane transverse (TO) motion parallel to quasi momentum of phonons nearer to K-point.⁴⁴ Here graphene possess a linear band structure which makes it to sufficiently vibrate with phonons that comes in and moves out. Heating and processing of graphite to form graphene may increase the oxidation and carbon-carbon overlapping that consequently decreases the intensity of bands in graphene. Also there was more rightward shift in bands of graphene when compared to graphite due to the in-plane stretching of sp^2 carbon atoms.⁴⁵ Morphology and atomic composition of graphite and graphene was shown in Figs. 4a, 4b respectively. The SEM image of graphene reveals the thin layered sheet structure comprising well bound layers of carbon atoms. The SEM image of graphite looks like a flaky multilayered structure with lots of agglomerated particles attached to the corners. EDX spectrum (Figs. 4a, 4b) reveals the composition of elements in graphene and graphite. It's evident that percentage of carbon increases in graphene owing to its purity. Also oxygen and Mn content slightly decreases

in graphene because of centrifugation and multiple times washing process.

Electrochemical studies.—Tafel polarisation studies were executed in both 6 M KOH and IG-6M KOH correlatively for Mg/a1, Mg/a2 and Mg/a3 electrodes. The lower potential limit and upper potential limit was set to -1.8 V and -1.0 V . Progressive drift in potential with respect to lower potential (-1.8 V) was observed as corrosion commenced with interval of 5 mV s^{-1} . Polarising potentiodynamic curves are shown in Figs. 4c, 4d. The corrosion potential (V_{corr}) value, extracted from polarisation curves shows the kinetics of corrosion getting diminished as -1.1 V , -1.33 V , -1.45 V and -1.59 V for Mg, Mg/a1, Mg/a2 and Mg/a3 in KOH electrolyte respectively. Similarly corrosion gets comparatively more lowered in IG-KOH electrolyte as -1.2 V , -1.53 V , -1.60 V and -1.66 V for Mg, Mg/a1, Mg/a2 and Mg/a3 respectively. Lower I_{corr} and more negative V_{corr} will exhibit minimal corrosion rate, which was evident in case of Mg/a3 based IG-KOH electrolyte. There exists a hierarchical lowering of corrosion rate in Mg/a1: Mg/a2: Mg/a3 respectively. Initially, high corrosion rates prevailed in plain Mg electrode as magnesium experienced a large hydrogen evaluation reaction due to reduction mechanism and conquered less negative potential ($\sim -1.1\text{ V}$). Also, reduction potential of magnesium was more negative than H_2 adopting easier reduction mechanism in Mg. This can be illustrated as,



Above reaction explains that Mg and water are simultaneously consumed to give out Mg(OH)_2 and H_2 . The prevailed corrosion in bare Mg electrode was substantially reduced by replacing Mg with

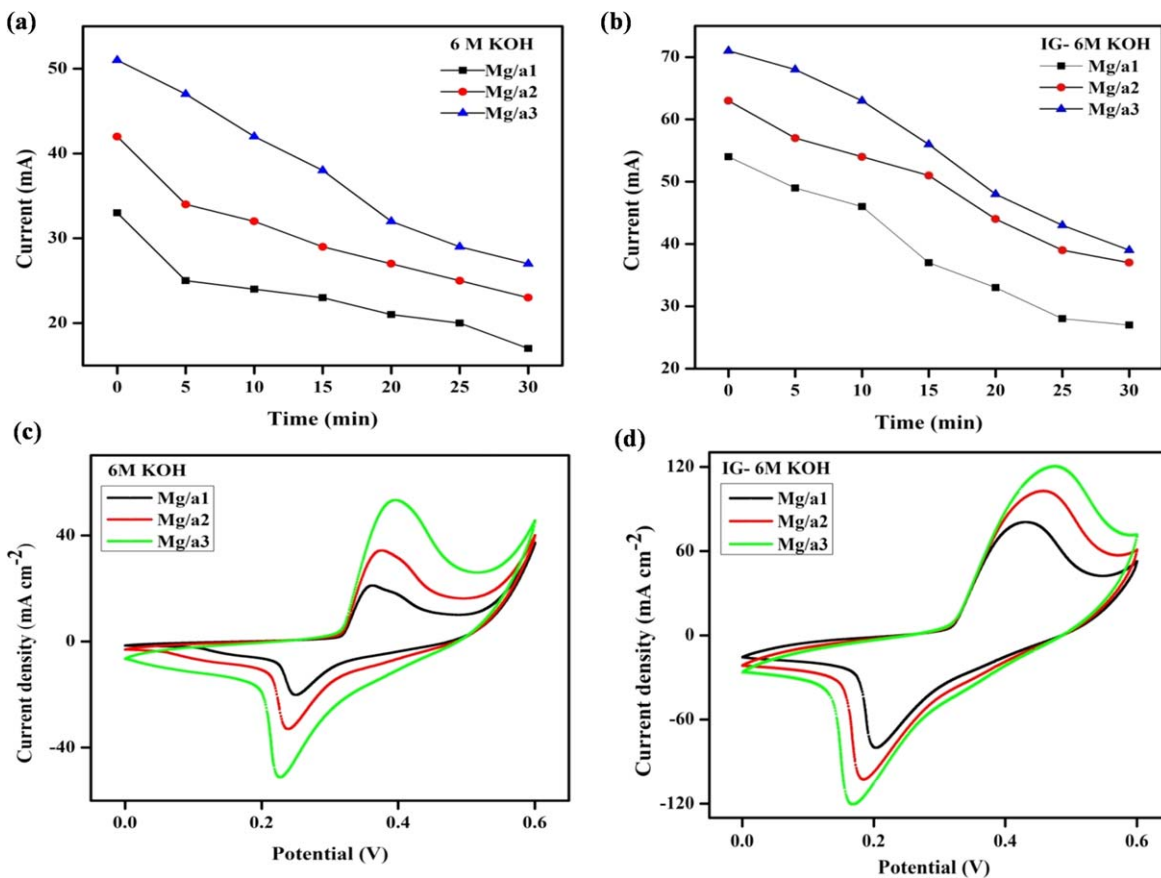


Figure 8 (a) Short-circuit studies of Mg/a1, Mg/a2 and Mg/a3 based air battery in 6 M KOH. (b) Short-circuit studies of Mg/a1, Mg/a2 and Mg/a3 based air battery in IG-6M KOH (c) Cyclic voltammetry studies in 6 M KOH. (d) Cyclic voltammetry studies in IG-6M KOH.

Mg/a1, Mg/a2 and Mg/a3 electrodes as they created a *solid electrolyte Interphase* (SEI) passivation layer above the Mg (OH)₂ layer reinforcing strong corrosion inhibition and controlling electrode-electrolyte interphase. But still there may be a very small existence of partial interaction between bare Mg electrode and electrolyte species, which doesn't have much influence on electrode performance. On deep exploration there comes the *barrier effect* offered by the perovskite coatings that guarded electrode-electrolyte interaction in order to improve performance and reduce corrosive effects. A synergetic effect inhibiting corrosion was observed in Mg/a3 and Mg/a2 electrode as proportionate concentration of calcium exists in higher orders ($x = 0.90$ and $x = 0.80$). This may be due to smaller nanocrystalline sizes and higher cross inter-linking density of the divalent Ca mixed barrier coatings that favoured high performance of electrode. IG-based Mg electrodes showed improved performance by less corrosive nature due to the reduced hydrophilic character or partial wetting and lesser diffusivity of corrosive species in the electrolyte.⁴⁶ Supporting SEM images of electrodes before and after polarisation studies shown in Fig. 5, provides facts about the mechanism of corrosion in both the electrolytes. SEM image of bare Mg electrode was found to be worn-out degrading as non-uniform corrosion at surfaces in both KOH and IG-KOH electrolytes. While Mg/a1, Mg/a2, Mg/a3 electrode surfaces intact possessed very minor cracks, degradation at lesser isolated areas that strongly conveys major electrode surfaces remain undamaged. From Fig. 5, it is clear that post polarisation studies in Mg/a2, Mg/a3 based IG KOH electrolyte had promising corrosion inhibition. The cathodic and anodic currents, corrosion rate were tabulated in Table I that redefines the better corrosion inhibiting performance of Mg/a3 electrode in both KOH and IG-KOH electrolyte. Simple preliminary test demonstrating surface coating durability was performed and the weight loss data with respect to time was tabulated in Table II. From

the Table II, it is evident that Mg/a3 showed lesser weight loss and improved durability in IG-KOH electrolyte. Also, polyvinylidene fluoride (PVDF) and N methyl 2 pyrrolidone are mostly inert and mostly do not resist corrosion⁴⁷ therefore the complete anticorrosive property is contributed by the prepared perovskite samples.

Electrochemical nyquist plots show the impedance performance of Mg/a1, Mg/a2 and Mg/a3 in KOH and IG-KOH electrolytes. Under the open circuit voltage of 1.48 V, the electrodes showed improved solution and charge transfer resistance for Mg/a3 followed by Mg/a2 and Mg/a1. low-frequency impedance correlated values were reported in Table III. The solution resistance and charge transfer resistance increases R_s —55.93%, 57.28%, 58.26% and R_{ct} —68.07%, 69.62%, 74.85% for respectively Mg/a1, Mg/a2 and Mg/a3 electrodes in IG 6 M KOH. The perovskite layers protect the electrode surface thereby limiting the flexible discharge of charges (e^-). Therefore, the resistance offered by charges during electrode-electrolyte interaction was improved. The nyquist graph shown in Figs. 6a, 6b depicts an increased semi-circular diameter with higher Z' for offered resistance.⁴⁸

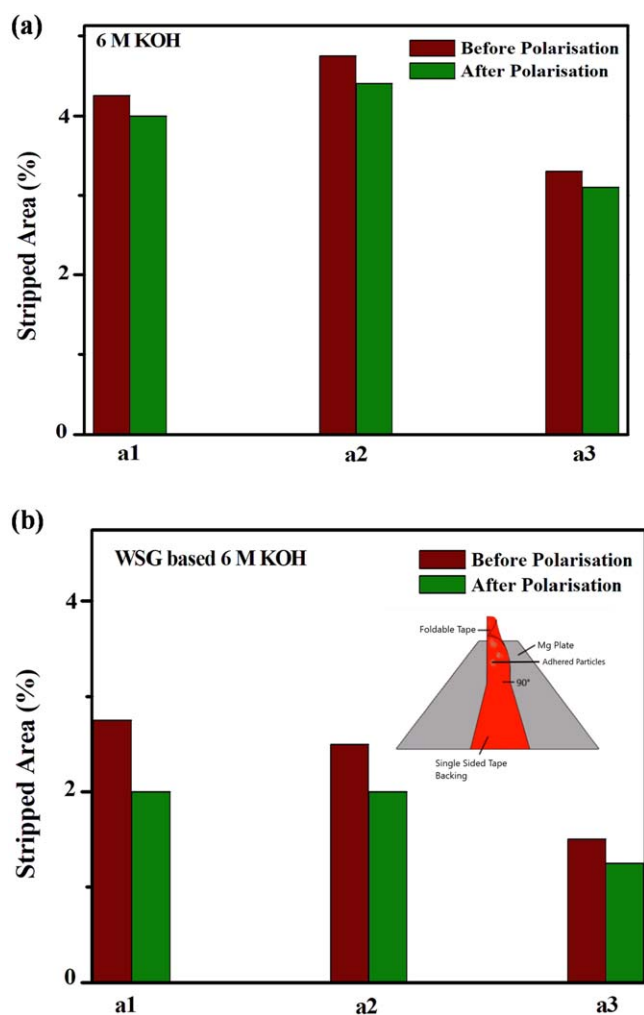
Construction and mechanism of Mg-air battery was shown in Figs. 7a–7c. The Fig. 7b demonstrates perovskite (0.3 g) layered Mg electrode, air gasping cathode with SS mesh and dual electrolyte medium KOH and IG-KOH. At constant current density of 5.66 mA cm⁻², separate discharge studies involving Mg/a1, Mg/a2 and Mg/a3 was executed in both the electrolytes (Figs. 7d, 7e). From the discharge plots life time in hours obtained for Mg/a1, Mg/a2 and Mg/a3, 6 M KOH based air battery are 5.57 h, 9.62 h and 9.86 h respectively. It is evident from Fig. 7d, 7e that the discharge performance and discharge time increases with increasing content of Ca. Figure 7e shows the well-improved battery life as 16.74 h, 21.17 h and 23.93 h for Mg/a1, Mg/a2 and Mg/a3 in IG 6 M KOH-air battery. The steep drop in Fig. 7e at constant current densities

Table IV. Short circuit study of Mg air battery in 6M KOH and IG-6M KOH electrolyte.

Duration (min)	Mg/a1 in 6M KOH			Mg/a2 in 6M KOH			Mg/a3 in 6M KOH		
	Voltage (V)	Current (mA)	Current density (mAcm ⁻²)	Voltage (V)	Current (mA)	Current density (mAcm ⁻²)	Voltage (V)	Current (mA)	Current density (mAcm ⁻²)
0	1.32	33	9.34	1.31	42	11.89	1.28	51	14.44
5	1.01	25	7.08	1.0	34	9.63	1.10	47	13.31
10	0.96	24	6.79	0.93	32	9.06	0.86	42	11.89
15	0.74	23	6.51	0.75	29	8.21	0.79	38	10.76
20	0.67	21	5.94	0.61	27	7.64	0.72	32	9.06
25	0.58	20	5.66	0.53	25	7.08	0.68	29	8.21
30	0.43	17	4.81	0.51	23	6.51	0.67	27	7.64
	Mg/a1 in IG-6M KOH				Mg/a2 in IG-6M KOH			Mg/a3 in IG-6M KOH	
0	1.09	54	15.29	1.05	63	17.84	0.96	71	20.11
5	0.75	49	13.88	0.73	57	16.14	0.78	68	19.26
10	0.60	46	13.03	0.68	54	15.29	0.61	63	17.84
15	0.54	37	10.48	0.52	51	14.44	0.54	56	15.86
20	0.35	33	9.34	0.47	44	12.46	0.51	48	13.59
25	0.22	28	7.93	0.44	39	11.04	0.47	43	12.18
30	0.20	27	7.64	0.35	37	10.48	0.43	39	11.04

Table V. Anodic and cathodic parameters obtained from cyclic voltammetry.

Specimen	Ipa (mA)	Ipc (mA)	Epa (V)	Epc (V)
6 M KOH				
Mg/a1	18.6	−14.5	0.3	0.23
Mg/a2	30.9	−24.3	0.37	0.22
Mg/a3	47.2	−36.1	0.39	0.21
IG-6 M KOH				
Mg/a1	65.5	−55.5	0.43	0.20
Mg/a2	87.0	−70.4	0.45	0.18
Mg/a3	97.1	−89.7	0.47	0.16

**Figure 9** (a) Adhesion test results in 6 M KOH (b) Adhesion test results in IG-6M KOH.

indicates the loss of activation mainly contributed by high oxygen reduction reaction (ORR) potential. The calculated discharge capacity of air battery in 6 M KOH without electrolyte additive was 371.3, 641.3 and 657.3 mAhg^{−1} at constant current density of 5.66 mA cm^{−2} for Mg/a1, Mg/a2 and Mg/a3 electrodes respectively. In order to maintain the electrolyte mixture to stay away from decomposition, the electrodes (anode and cathode) must possess a electrochemical potential in between the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of the corresponding electrolyte. In our case, the electrochemical potential of Mg electrode was over head to the LUMO of the electrolyte, causing electrode corrosion and decomposition.

Perovskite layered electrode acts as a SEI passivation layer above the Mg(OH)₂ layer thereby partially restricting electrode-electrolyte interaction. Bare Mg electrode reacts with electrolyte and forms Mg(OH)₂ layer over its surface. However, poor chemical stability of Mg(OH)₂ layer makes it to dissolve in the electrolyte. There exists a continuous action of re-forming and consuming Mg(OH)₂ layer in bare Mg electrode reducing the air battery performance. In contradiction, Mg/a1, Mg/a2 and Mg/a3 electrodes form stable protective SEI layer on the electrode surface, enhancing the performance of air battery. The operating life of Mg anode was increased by 33.53% (a1), 41.44% (a2), and 42.1% (a3) hierarchically while increasing the Ca content, as faster reaction kinetics and predominant lowering of polarising nature in Ca²⁺ is eminent than Mg²⁺. Also, Mg/a3 air battery has better operating characteristics due to the small crystallite site of a3, providing more active surface sites. The discharge capacity of Mg-air battery in 6 M KOH with IG electrolyte additive gets tremendously enhanced to 1116.2, 1411.3, 1595.3 mAhg^{−1}, for Mg/a1, Mg/a2 and Mg/a3 electrodes respectively. Transformation of OH[−] with IG particles from the electrolyte will possibly be deposited in the electrode interfacial surface acting as a protective barrier and active catalysts improving battery characteristics. Gradual decrement in voltage and stretched increment in discharge plateau shows better discharge capacity of IG based Mg-air battery. Meanwhile, an abrupt change in voltage observed in Mg-air battery without additive shows less discharge capacity evident in Fig. 7d. This observation makes it clear that electrode-electrolyte interfacial protective layer over the Mg anode in IG based air-battery maintains at most a constant current conductance thereby extraordinarily improving the battery performance. It's notable that for the first time, the combination of La_{1-x}Ca_xMnO₃ perovskite electrode-electrolyte protective passivation layer and interspersed graphene electrolyte additive together studied for the mind-blowing betterment of the Mg–O₂ battery characteristics. On the other hand, oxidation reduction reactions (ORR) at air cathode consume water and oxygen and produce hydroxide ion.⁴⁹ The hydroxide (OH[−]) ions get transported and patch-up the OH[−] consumed at anode. Oppositely, water gets generated at anode-electrolyte interface gets transferred across the battery and restores water consumed by the cathode.

Short circuit studies were demonstrated for Mg/a1, Mg/a2 and Mg/a3 electrodes in both the electrolytes shown in Figs. 8a, 8b. Table IV displays the short circuit current, current density and voltage measured for self-discharge curves over 0.5 h during the studies. There was an apparent change in the plot of IG based air battery exhibiting a decrease in discharge current from 54 to 27 mA for Mg/a1, 63 to 37 mA for Mg/a2 and 71 to 39 mA for Mg/a3. Meanwhile the discharge plateau decreased from 33 to 17 mA for Mg/a1, 42 to 23 mA for Mg/a2 and 51 to 27 mA for Mg/a3 in 6 M KOH air battery. Incredible percentage of improvement (61.08%) was observed in comparing the discharge drain current of IG KOH and KOH electrolytes. It was assumed that lowered self-corrosion rate and breakdown of anode was prohibited due to the electrode barrier coating.⁵⁰

The cyclic voltammetry (CV) curves obtained for Mg/a1, Mg/a2 and Mg/a3 electrodes in both the electrolytes after 20th cycle was presented in Figs. 8c, 8d. The electrode adsorption was predominant in IG based Mg electrodes due to the passivation layer formation on the electrode surface by the accumulating action of oppositely charged ions and improved surface area. Larger potential areas were trapped for Mg/a3 in both the electrolytes because of the surface oxidation-reduction reaction prevailing over larger surface area of electrode. Presence of more oxygen functionalities over the surface of Mg/a3 allows having higher mass-transfer resistance and improved potential. Overall, the performance of Mg/a3-IG electrode-electrolytes was enhanced significantly, due to their larger surface area, better structural density and stability.^{51,52} The increased oxidation-reduction potentials for Mg/a3 was due to the formation of LCMO intercalated carbon interfacial layers over the Mg electrode surface. The anodic and cathodic parameters for Mg/a1, Mg/a2 and Mg/a3 are listed in Table V.

Adhesion studies.—Adhesion test performed on Mg/a1, Mg/a2 and Mg/a3 electrodes displayed analogous increase in adhesion rate by flourishing 4B (0%–5%) peeling rate under ASTM standards.⁴⁷ Mg/a3 accounts for good adhesiveness and high durability of coating by showing lesser peel-off rate. Figure 9. shows the better adhesive nature of Mg/a3 in both KOH and IG-KOH electrolytes. This strong adhesion may be considered due to the cohesive forceful intercalation of perovskites and PVDF matrix over the surface of the electrodes. Among the electrodes, Mg/a3 showed better adhesive nature due to its lower crystallite size and higher packing density.

Conclusions

Polar interspersed graphene was successfully prepared from waste dry cell electrodes, encouraging “Best out of waste” strategy, so as to reduce the local accumulation of solid battery waste. Structural, morphological, compositional and surface area analysis for the perovskite material, $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ and graphene was discussed. The anticorrosive property of perovskite magnetite material, $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ increases on increasing the content of calcium due to its lesser crystallite size. Polar interspersed graphene played a significant role as a catalyst, anodic breakdown protector and as a corrosion inhibitor in 6 M KOH electrolyte. The IG-Mg air battery with $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.90$) electrode coating achieved excellent discharge capacity 1595.3 mAhg^{-1} that was 55.7% efficient than regular Mg air batteries (890 mAhg^{-1}). Hence, the IG based Mg air battery with $\text{La}_{0.10}\text{Ca}_{0.90}\text{MnO}_3$ anodic coating offered sustained long shelf life, less anodic corrosion improved battery performance and is recommended to be used in modern electric vehicles. Nonetheless, there is tremendous future scope for further optimisation of electrolytes and electrode materials, especially towards suppression of anodic corrosion in metal-air batteries. The concept of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ coating and IG electrolyte additive can be extended to other types of energy technologies specifically to air-battery systems.

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References

- X.-J. Gu, W.-L. Cheng, S.-M. Cheng, H. Yu, Z.-F. Wang, H.-X. Wang, and L.-F. Wang, *J. Electrochem. Soc.*, **167**, 020501 (2020).
- N. Zhang, S. Xie, W. Wang, D. Xie, D. Zhu, and F. Cheng, *J. Electrochem. Soc.*, **167**, 020505 (2020).
- C.-S. Li, Y. Sun, F. Gebert, and S.-L. Chou, *Adv. Energy Mater.*, **7**, 1700869 (2017).
- N. Nakatani, K. Kishida, and K. Nakagawa, *J. Electrochem. Soc.*, **165**, A1621 (2018).
- L. E. Erickson, *Environ Prog Sustain Energy*, **36**, 982 (2017).
- Y. Li and J. Lu, *ACS Energy Lett.*, **2**, 1370 (2017).
- Z. L. Wang, D. Xu, J. J. Xu, and X. B. Zhang, *Chem. Soc. Rev.*, **43**, 7746 (2014).
- F. Cheng and J. Chen, *Chem. Soc. Rev.*, **41**, 2172 (2012).
- M. A. Rahman, X. Wang, and C. Wen, *J. Electrochem. Soc.*, **160**, A1759 (2013).
- J. Christensen, P. Albertus, R. S. Sanchez-Carrera, T. Lohmann, B. Kozinsky, R. Liedtke, J. Ahmed, and A. Kojic, *J. Electrochem. Soc.*, **159**, R1 (2011).
- S. S. Suren and S. Kheawhom, *J. Electrochem. Soc.*, **163**, A846 (2016).
- T. Zhang, Z. Tao, and J. Chen, *Mater. Horiz.*, **1**, 196 (2014).
- J. Mei, T. Liao, J. Liang, Y. Qiao, S. X. Dou, and Z. Sun, *Adv. Energy Mater.*, **10**, 1901997 (2020).
- W. Li, C. Li, C. Zhou, H. Ma, and J. Chen, *Angew. Chem. Int. Ed.*, **45**, 6009 (2006).
- R. Chen, R. Luo, Y. Huang, F. Wu, and L. Li, *Adv. Sci.*, **3**, 160051 (2016).
- T. W. Cain, I. Gonzalez-Afanador, N. Birbilis, and J. R. Scully, *J. Electrochem. Soc.*, **164**, C300 (2017).
- S. Bender, J. Goellner, A. Heyn, and S. Schmigalla, *Mater. Corros.*, **63**, 707 (2012).
- U. Gopalakrishna Bhat and K. Vamsee, *Sci. Total Environ.*, **134**, 887 (1993).
- A. Rao, K. R. Rupesh, F. Ehrenhauser, K. Nandakumar, L. J. Thibodeaux, D. Rao, and K. T. Valsaraj, *Can. J. Chem. Eng.*, **92**, 2098 (2014).
- Z. Zhu, Q. Sun, Z. Zhang, J. Dai, G. Xing, S. Li, X. Huang, and W. Huang, *J. Mater. Chem. C*, **6**, 10121 (2018).
- R. Alagheband, S. Maghsoodi, A. S. Kootenaei, and H. Kianmanesh, *Bull. Chem. React. Eng. Catal.*, **13**, 47 (2018).
- S. Chopra, S. Sharma, T. C. Goel, R. Chatterjee, and R. G. Mendirattat, *Comput. Mater.*, **37**, 134 (2006).
- M. Mamak, G. S. Métraux, S. Petrov, N. Coombs, G. A. Ozin, and M. A. Green, *J. Am. Chem. Soc.*, **125**, 5161 (2005).
- H. Jie, L. Wang, L. Shi, and H. Huang, *J. Power Sources*, **269**, 144 (2014).
- L. S. Roselin, R.-S. Juang, C.-T. Hsieh, and S. Suresh, *Materials*, **12**, 1229 (2019).
- K. Chen, Q. Wang, Z. Niu, and J. Chen, *J. Energy. Chem.*, **27**, 12 (2018).
- W. Wan, X. Zhu, X. He, Y. Wang, Y. Yan, Y. Wu, and Z. Lü, *J. Electrochem. Soc.*, **165**, A1741 (2018).
- M. J. Allen, V. C. Tung, and R. B. Kaner, *Chem. Rev.*, **110**, 132 (2010).
- N. Parhizkar, B. Ramezanzadeh, and T. Shahri, *J. Electrochem. Soc.*, **164**, C1044 (2017).
- Q. Cheng, Y. Okamoto, N. Tamura, M. Tsuji, S. Maruyama, and Y. Matsuo, *Sci. Rep.*, **7**, 14782 (2017).
- M. Alaf, U. Tocoglu, M. Kartal, and H. Akbulut, *Appl. Surf. Sci.*, **380**, 185 (2016).
- Z.-S. Wu, W. Ren, L. Gao, and J. Zhao, *ACS Nano*, **3**, 411 (2009).
- W. Choi, I. Lahiri, R. Seelaboyina, and Y. S. Kang, *Crit. Rev. Solid State Mater. Sci.*, **35**, 52 (2010).
- G. Ji, W. Zhao, J. Wei, L. Yan, Y. Han, Q. Luo, S. Yang, J. Hou, and C.-Q. Ma, *J. Mater. Chem. A*, **7**, 212 (2019).
- A. I. Kontos, A. G. Kontos, D. S. Tsoukleris, M.-C. Bernard, N. Spyrellis, and P. Falaras, *J. Mater. Process. Technol.*, **196**, 243 (2008).
- M. Topsakal, H. Şahin, and S. Ciraci, *Phys. Rev. B*, **85**, 155445 (2012).
- M. Arunachalam, P. Thamilmaran, S. Sankararajan, and K. Sakthipandi, *Physica B*, **456**, 118 (2015).
- H. Yang and P. Jiang, *Langmuir*, **26**, 12598 (2010).
- N. I. Zaaba, K. L. Foo, U. Hashima, S. J. Tanb, W.-W. Liu, and C. H. Voona, *Procedia Eng.*, **184**, 467 (2017).
- S. Seonho, H. Park, and J. Kim, *Micromachines*, **11**, 605 (2020).
- D. Das, C. M. Srivastava, D. Bahadur, A. K. Nigam, and S. K. Malik, *J. Condens. Matter Phys.*, **16**, 4089 (2004).
- D. L. Flor, D. O. Gemma, R. A. Evarestov, Y. E. Kitaev, E. Tasci, and M. I. Aroyo, *J. Appl. Crystallogr.*, **52**, 1214 (2019).
- K. Kishore Kumar, R. Brindha, M. Nandhini, M. Selvam, K. Saminathan, and K. Sakthipandi, *Ionics*, **25**, 1699 (2019).
- G. Li, Y. Xia, Y. Tian, Y. Wu, J. Liu, Q. He, and D. Chen, *J. Electrochem. Soc.*, **166**, B881 (2019).
- Y. Obeng and P. Srinivasan, *J. Electrochem. Soc. Interface*, **20**, 47 (2011).
- P. M. Barkhudarov, P. Shah, E. Watkins, and D. A. Doshi, *Corr. Sci.*, **50**, 897 (2008).
- R. Brindha, M. Nandhini, S. S. R. Ajith, M. Selvam, K. Subannajui, K. Khotmunkhun, and K. Sakthipandi, *Bull. Mater. Sci.*, **42**, 221 (2019).
- M. T. Rahmana and C. V. Ramana, *J. Appl. Phys.*, **116**, 164108 (2014).
- C. F. Liu, Z. G. Neale, and G. Cao, *Mater. Today Commun.*, **19**, 109 (2016).
- J. Balaji and M. G. Sethuraman, *RSC Adv.*, **6**, 95396 (2016).
- Z. Yu, LaureneTetard, L. Zhai, and J. Thomas, *Energy Environ. Sci.*, **8**, 702 (2015).
- S. J. R. Prabakar, Y.-H. Hwang, E. G. Bae, and D. K. Lee, *Carbon*, **52**, 128 (2013).