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Urea Assisted Combustion Synthesis of LiFePO$_4$/C Nano composite Cathode Material for Lithium Ion Battery Storage System

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Abstract

In the present work, we demonstrated economical way to synthesize nano crystalline LiFePO$_4$ Olivine structured LiFePO$_4$/C nanocomposite using urea as fuel and sucrose as carbon source were calculated using the total oxidizing and reducing valencies of the components which provide as numerical coefficients for stoichiometric balance so that the equivalent ratio is unity followed by heat treatment at 600 ºC for 6 - 10 h, under Ar (90%) and H2 (10%) gas atmosphere. The resultant products are characterized by XRD to know the phase formation and for estimation of the crystallite size. The XRD patterns were collected in steps of 0.02° over the range of 10° ≤2θ ≤80° at room temperature with a constant counting time of 0.1 s per step , From XRD all the powders showing the nano sized crystallite sizes in the range of 40-45nm. The morphologies of the powders were investigated by a scanning electron microscopy (SEM) all samples indicate the agglomeration of powder with highly porous nature in all the samples. The synthesized olivine powders were subjected to thermogravimetric / differential scanning calorimetry (TG-DSC) as the reference material in the temperature range of 25–1000°C with a heating rate of 10°C/min in air and nitrogen atmosphere. Raman spectra were obtained with 514.5 nm Ar-Ion laser radiation at a laser power of 150 mW in the range of 100- 2000cm^{-1} for a total of 10 scans to increase the signal-to-noise ratio and with 4 cm^{-1} spectral resolution were studied.
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1. Introduction

With the entrance into the 21st century, our society has changed into an information-rich society. All kinds information fill our daily life up. Lithium ion battery are become the battery of choice in large scale applications, because of their high energy density. The cathode material, plays an virtual role in lithium ion battery Li-ion batteries are often selected as a power supply for these high-tech products. $LiFePO_4$ is one of the most promising candidates among the large number of Fe-related compounds due to its high energy density (theoretical capacity: about 170mAhg[-1]; working voltage: 3.5 V) Low electronic conductivity has been considered as the main problem of $LiFePO_4$ [1]. During charge process, the extraction of lithium from $LiFePO_4$ is accompanied by a direct transition to $FePO_4$, [2] in which Fe2+ ions are oxidized to Fe3+. Both $LiFePO_4$ and $FePO_4$ are poor electronic conductors[3] since there is no mixed - valent cations in these two phases, thereby caused poor electronic conductivity of $LiFePO_4$ electrode[4]. Thus, Li ions can only partially extracted / inserted at room temperature at modest rates[5]. In order to obtain high power output[6], many methods have been carried out to overcome this limitation[7], including carbon coating [8] or Ag coating [9] [10]etc.
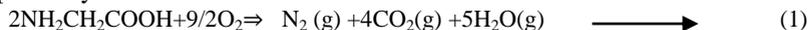
In this paper we are presenting a economical and simple Combustion bottom up method to synthesize $LiFePO_4$/C Nano composite material as cathode for lithium ion battery. In the present study, we have developed urea assisted combustion method, with sucrose is used in the initial stages as carbon source as well as reducing agent. This process is simple and inexpensive route for obtaining $LiFePO_4$/C material and has great potential from the commercial point of view. Here in this report we demonstrate Urea-to-Nitrate molar ratio for various molarities, the heat treated $LiFePO_4$/C powder thus processed displays a well-developed olivine crystalline structure and shows best electrochemical performance.
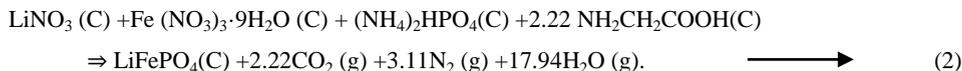
2. Experimental

2.1 Combustion reactions:

The corresponding chemical reaction is as follows:

[1]. One mole of NH_2CONH_2 and NH_2CH_2COOH are as fuels, gave four and five moles of the following gases as per the reactions respectively.

$$2NH_2CH_2COOH+9/2O_2 \Rightarrow N_2\,(g) +4CO_2(g) +5H_2O(g) \longrightarrow \quad (1)$$

[2]. Theoretical equations for producing $_{LiFePO4}$ by using urea are.

$$LiNO_3\,(C) +Fe\,(NO_3)_3 \cdot 9H_2O\,(C) + (NH_4)_2HPO_4(C) +2.22\,NH_2CH_2COOH(C)$$

$$\Rightarrow LiFePO_4(C) +2.22CO_2\,(g) +3.11N_2\,(g) +17.94H_2O\,(g). \longrightarrow \quad (2)$$

In all experiments, the fuel-oxidizer ratio was set to unity; i.e., enough oxidizer was present to fully oxidize the fuel with no required contribution of atmospheric oxygen.To observe the variation in adiabatic flame temperature with fuel-to-nitrate molar ratio, adiabatic flame temperatures were also calculated for nitrate-to-Urea molar ratios. The combustion reactions involving these ratios can be presented above equation (1) & (2). Calculation based on thermodynamic considerations help in predicting the exact situations for initiation and ignition of reactions. Adiabatic flame temperature T_{ad}, is used to define the temperature at which the enthalpies of the products are equal to those of reactants.

T_{ad} can be calculated using the following equations:

The Enthalpy of combustion can be expressed as:

$$\Delta H^0_{reaction}= (\sum n\Delta H^0_f)_{\text{products}} - \sum (n\Delta H^0_f)_{\text{reactants}} \longrightarrow \quad (3)$$

Adiabatic flame temperature can be calculated by using the equation:

$$Q = -\Delta H^0_{reaction} = \int_{298}^{T_{ad}} (\sum nC_p)_{products} dT \longrightarrow \quad (4)$$

Where n is the number of the mol and T_{ad} is the adiabatic flame temperature. Using the thermodynamic data for various reactants and products the enthalpy of combustion and the theoretical adiabatic flame temperatures as a function of urea-to-nitrate molar ratio can be calculated.

2.2 Calculation of Fuel- to-Nitrate ratio for Urea:

General chemical formula is:

$LiNO_3$ (C) +Fe $(NO_3)_3 \cdot 9H_2O$ (C) + $(NH_4)_2HPO_4$(C) +-------- NH_2CONH_2 (C)

$$\Rightarrow LiFePO_4(C) + ------CO_2 \text{ (g)} + --------N_2 \text{ (g)} + ---------H_2O \text{ (g)}. \longrightarrow \quad (5)$$
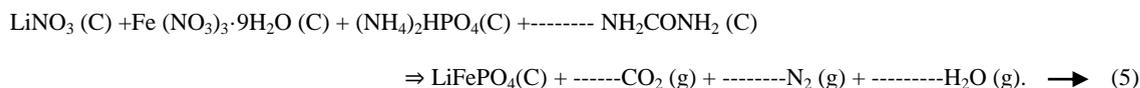
The corresponding stoichiometric chemical reaction is as follows:

$LiNO_3$ (C) +Fe $(NO_3)_3 \cdot 9H_2O$ (C) + $(NH_4)_2HPO_4$(C) +*3.33* NH_2CONH_2 (C)

$$\Rightarrow LiFePO_4(C) + 3.33CO_2 \text{ (g)} + (2 + 3.33) N_2 \text{ (g)} + (13.5 + 3.33 \times 2)H_2O \text{ (g)}. \longrightarrow (6)$$

From this chemical reaction nitrate to urea molar ratio is
Nitrates have **3.33** *Urea i.e.,*

$$\frac{F}{N} = \frac{Fuel}{Oxidant} = \frac{Fuel}{Nitrate} = \frac{\boldsymbol{Urea}}{\boldsymbol{Nitrate}} = \frac{3.33}{4} = 0.8325 \quad \longrightarrow \quad (7)$$

Table 1. Urea-to-Nitrate molar ratio for various molarities

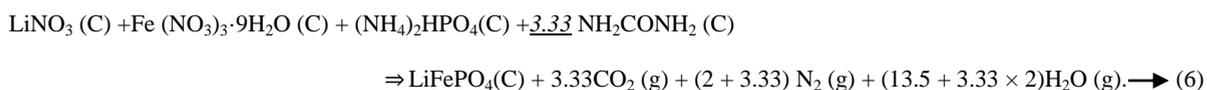| Metal	Fuel	molar ratio	Nitrate/Urea	Enthalpy of combustion	
				$\Delta H_{reaction}^0$	T_{ad}
Nitrate	Urea	(1:1:1)	0.25	1034.57kcal/mol	0.0302°K
Nitrate	Urea	1:1:2	0.50	490.49kcal/mol	1.277°K
Nitrate	Urea	1:1:3	0.75	−53.57kcal/mol	601°K
Nitrate	Urea	1:1:3.3	0.8250	−216.79kcal/mol	1043°K
Nitrate	Urea	1:1:4	1	−595.85kcal/mol	2001°K
Nitrate	Urea	1:1:5	1.25	−1141.71kcal/mol	2952°K
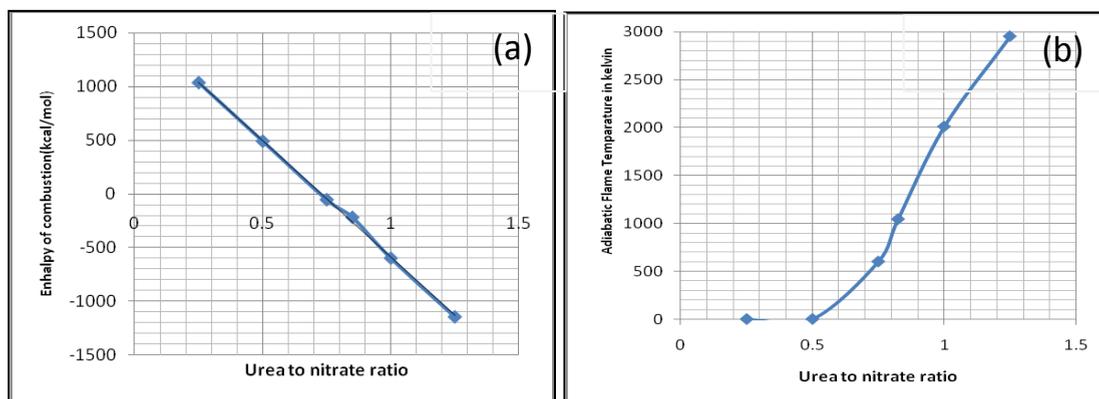
Fig. 1. (a)Enhalphy of combustion (k cal/mol) Vs Urea to nitrate ratio.(b) Adiabatic flame temperature in kelvin Vs Urea to nitrate ratio.

Synthesis

In a typical combustion synthesis the stoichiometric amounts of $LiNO_3$, $Fe(NO_3)_3 9H_2O$, $(NH_4)_2HPO_4$ and urea (ratio of fuel and nitrate) were calculated using the total oxidizing and reducing valencies of the components which provide as numerical coefficients for stoichiometric balance so that the equivalent ratio is unity and the energy

generated by the combustion is at a maximum. These precursors mixed in beaker to make paste. After addition of required amount of sucrose as a carbon source (10-30%), the mixture was heated on a preheated hot plate of temperature (∽400°C). Within a few minutes of heating, reaction mixture was converted into a red colour viscous liquid and started boiling. The viscous liquid was swelled and auto-ignited with the evolution of a large volume of gases in different fashion, depending on the fuel-to-oxidant ratio. At this higher temperature the metal nitrate decomposed to metal oxides and oxides of nitrogen .Two particular starting fuel -to- oxidant ratios were selected in the present work. In case, where the amount of fuel was adjusted according to the principle of propellant chemistry[10] nitrate-to-urea molar ratio. 1:3.33) upon auto-ignition resulted in a black colour voluminous product. After about 3 min of heating, the concentrated mixture solution burst into flames and resulted into a foamy black powder. The obtained precursor powders were mixed thoroughly in a mortar and cold pressed into cylindrical pellets of 10 mm diameter and about 6 mm height using an manual uniaxial hydrolic press at a compaction pressure of 0.5 ton and heated in tubular furnace and vacuum furnace under flowing 90%Ar and 10% of H_2 gas at 600°C for 6-10 h, and then air-cooled to room temperature in order to obtain pure and well crystallized $LiFePO_4/C$ powders.

3.CHARECTARIZATION

3.1 .X-Ray Diffraction analysis :

XRD patterns were recorded using Cu-Kα (λ = 1.5418 Å (in 2θ)) radiation on a X-ray diffraction (XRD, Bruker D8-advance, Germany) to know the phase formation and for estimation of the crystallite size. The XRD patterns were collected in steps of 0.02° over the range of 10° ≤2θ ≤80° at room temperature with a constant counting time of 0.1 s per step.All reflections can be indexed based on the orthorhombic $LiFePO_4$ crystallizing in the space group *Pnma* with JCPDS card No: 00-40-1499 The unit cell parameters obtained for $LiFePO_4/C$ (a = 10.3281 A°, b = 6.0080 A°, c = 4.6947A°) and for $LiFePO_4/C$(a = 10.3314 A° , b = 6.0064 A° , c = 4.6996 A°) are in a good agreement with the

Fig.2. XRD patterns of samples (a) standard $LiFePO_4$ with JCPDS card No:00-40-1499 (b) with Urea and 10% glucose

(c) with Urea and 20% glucose powders heat treated at 600°C for 7 hrs in vacuum furnace.

However, main peaks sharpen upon increasing the heating time, indicating that increase in crystalinity may be a result of growth of grain size, well ordered structure, and release of lattice strain. X-ray diffraction patterns of various powders synthesized in this study by using urea the XRD obtained by the combustion of lithium nitrate, ferric nitrate, Di-Ammonium orthophosphate, urea and 10% of sucrose as carbon source and calcinated at 600 C for 7h in vacuum, exhibiting the XRD peaks indicative of single phase $LiFePO_4$ and very fine crystallite size calculated from Debye-Scherrer's formula is 42nm. Fig.2. XRD of the $LiFePO_4$, same as above but with 20% of sucrose to the final product. This is also showing single phase $LiFePO_4$. But the figure 2b & c showing the impurity phases

corresponding to LiFe(P_2O_7), $Li_3Fe_2(PO_4)_3$ and Li3PO4 in addition to $LiFePO_4$.These impurity phases are formed due to the insufficient quantity of reducing material i.e carbon which is used as carbon source and also may be due to vacuum heat treatment. All the powders showing very fine crystallite sizes. ones reported in literature.

3.2. Microstructure

The morphologies of the powders were investigated by a scanning electron microscopy (SEM) (Hitachi S-3400E/N)
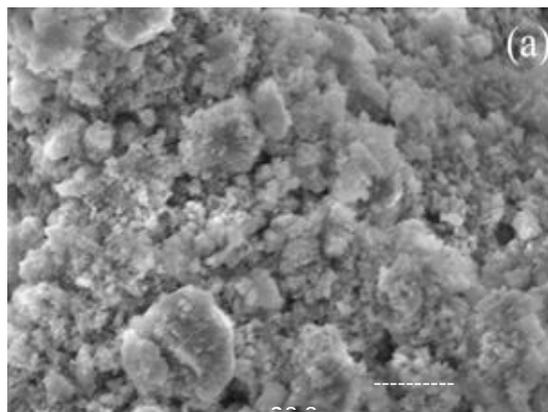
Fig. 3. SEM images of $LiFePO_4$/C composites containing samples

S1-Sample urea as fuel with 10% glucose and calcinated at 600C for 8 hrs in 90%Ar and 10% H2,

In Fig. 3 shows the scanning electron micrographs of carbon coated $LiFePO_4$ which are calcinated in vacuum for 7hrs. The SEM pictures indicate the agglomeration of powder with highly porous nature in all the four cases. From XRD all the powders showing the nano sized crystallite sizes in the range of 40-45nm.

3.4.TG–DSC analysis of combustion synthesized powders in static atmosphere:

The synthesized olivine powders were subjected to thermogravimetric/ differential scanning calorimetry (TG-DSC) on a Netzch (Luxx, STA, 449 Jupiter, Germany).Thermogravimetric–differential scanning calorimetry (TG-DSC) was used to establish the calcination temperature for pure $LiFePO_4$ phase formation. Fig.4(a) and 4(b) shows the TG–DSC analysis curves for the combustion synthesized carbon coated $LiFePO_4$ by using as fuel in static atmosphere at a heating rate of 10°C/min. The TG curves indicate one slight mass-loss peak between 50 and 80°C. This mass-loss process is related to endothermic peaks in the DSC curves, due to evaporation of moisture, which is absorbed by the sample. Because these powders are highly hydroscopic. An endothermic peak has been observed at 436°C for pure $LiFePO_4$, but no appreciable weight loss is observed in the TG curve for the sample. The broad exothermic peak at 436-601°C, suggesting that the crystallization of $LiFePO_4$ takes place at this temperature. The exothermic peaks observed around 600-700°C correspond to the decomposition of $LiFePO_4$ which is formed. Further increasing the temperature these powders melted at the temperature 889 and 890°C . In the case of combustion synthesized powders above 600°C there is a mass change, due to decomposition of crystalline $LiFePO_4$ which is formed below 600°C.

TG–DSC analysis of combustion synthesized powders in Nitrogen atmosphere:

Fig.5(a) & 5(b) shows the TG-DSC of the as synthesized powders before calcination. This is performed in nitrogen atmosphere at heating rate of 10°C/min by flowing the nitrogen at a rate of 60ml/min. Fig.5(a) shows that there is slight mass change in combustion synthesized powders around 7 and 10 urea respectively. An endothermic peak has been observed at 436°C for pure $LiFePO_4$, but no appreciable weight loss is observed in the TG curve for sample. The broad exothermic peak at 436-550°C, suggesting that the crystallization of $LiFePO_4$ takes place at this temperature. The exothermic peaks observed around 600-700°C correspond to the decomposition of $LiFePO_4$ which is formed. The endothermic peak around 756°C in sample corresponding to formation of Fe_2P, which is impurity generally formed in $LieFePO_4$.
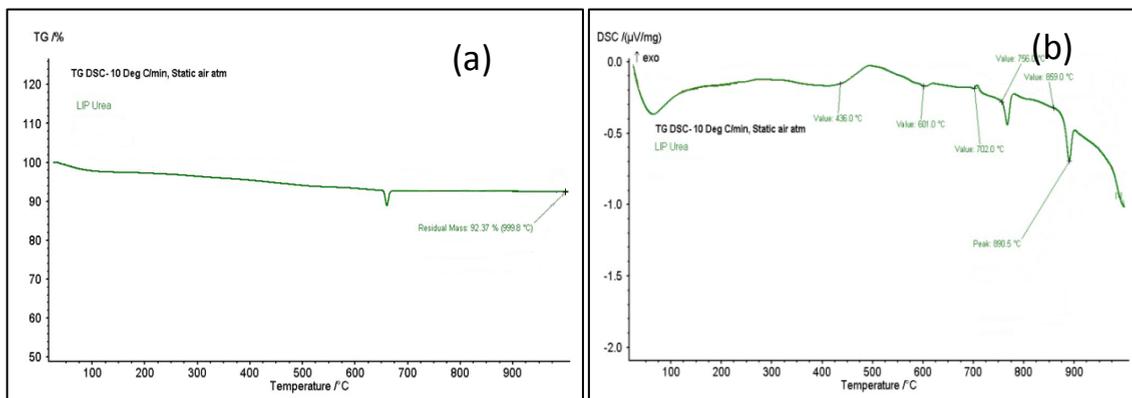
Fig.4.(a). Thermogravimetry of combustion synthesized powders (b). Differential scanning calorimetry of combustion synthesized powders
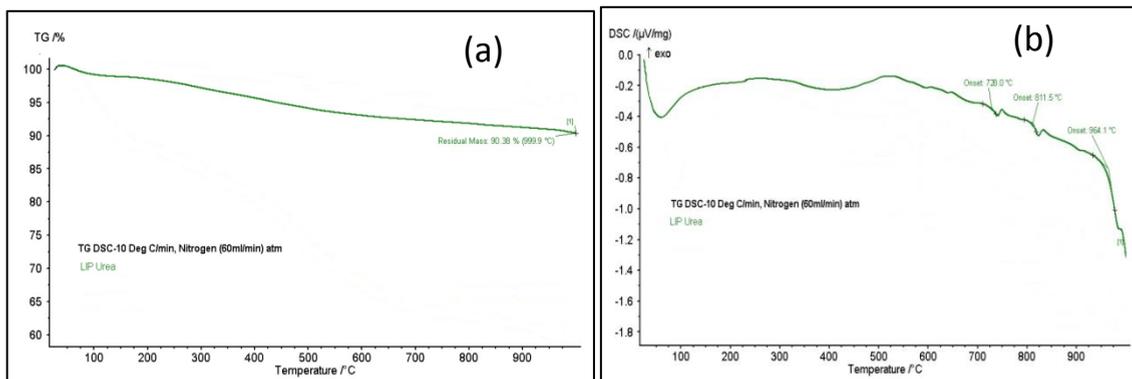

Fig.5 (a). Thermogravimetry of combustion Synthesized powders (b). Differential scanning calorimetry of combustion synthesized powders

3.5. Raman spectroscopy

Raman spectra were obtained from a Horiba Jobin-Yvon Labram HR 800 Raman spectrometer with 514.5 nm Ar-Ion laser radiation at a laser power of 150 mW in the range of 100- 2000cm^{-1} for a total of 10 scans to increase
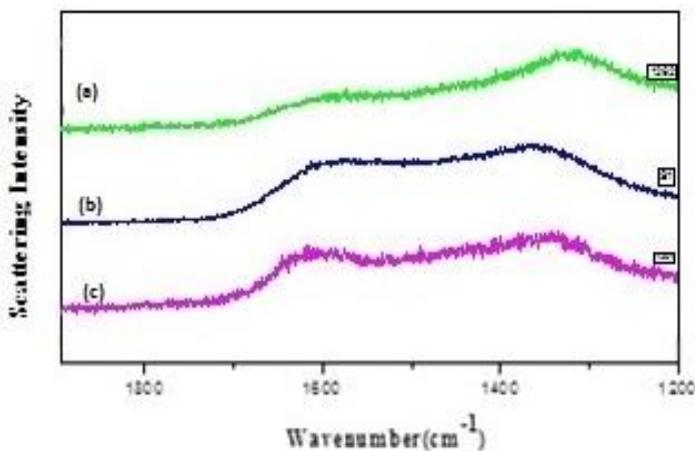

Fig.6 Raman spectrum of six samples (a) Urea+10%Glucose+HT600°C 6h (b)Urea+10%Glucose+VT600°C7h

(c) Urea+20%Glucose+VT600°C 7h

the signal-to-noise ratio and with 4 cm^{-1} spectral resolutionThe structure of the surface coated carbon and the material were investigated by Raman spectroscopy. It is well known that the Raman spectra of amorphous carbons exhibit broad bands in the 1000~1700 cm^{-1}, and the peaks having the maxima in the 1300~1400 cm^{-1} and 1550~1650 cm^{-1} are called the D-band and G-band, respectively.The Raman spectra of all samples display two broad peaks at 1300-1480 and 1600-1625 cm^{-1}, both of which were attributed to the D band (disordered carbon, sp^3) and the G band (graphite, sp^2) of Raman vibration modes for amorphous carbon, respectively. Two broad peaks cantered at about 1345 and 1620 cm^{-1} corresponds to the D and G bands which show a breathing mode of rings and vibrations of sp^2 carbon atoms with dangling bonds, respectively.

4.Conclusion

The nanocrystalline LiFePO$_4$/C nanocomposite material was successfully synthesized by a urea and sucrose modified combustion process, sucrose used as carbon source to increase electronic conductivity and in the initial stages it reduces the ferric to ferrous state. The heat treated samples improves pure and crystallinity of the as prepared sample. The LiFePO$_4$/C sample shows nano porous morphology with the nano crystallite sizes in the range of 40-45nm. With spherical shape morphology, XRD pattern of LiFePO$_4$/C Nano composite clearly reveals the crystalline orthorhombic. Raman spectra of amorphous carbons exhibit broad bands and the peaks of D-band and G-band, respectively. TG–DSC analysis**,** An endothermic peak has been observed at 436°C for pure LiFePO$_4$, but no appreciable weight loss is observed in the TG curve for the sample. The broad exothermic peak at 436-601°C, suggesting that the crystallization of LiFePO$_4$ takes place at this temperature. The exothermic peaks observed around 600-700°C correspond to the decomposition of LiFePO$_4$ which is formed. This can be used as cathode for Lithium ion batteries. It can increase temperature stability of the battery and avoid spilling, boiling or gassing of the batteries. Thus, we can increase safety of the battery. This method is simple, efficient, economical, environment friendly, and has great potent from commercial point of view.

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