



RESEARCH ARTICLE

DOPING DEPENDENCE OF OPTICAL AND ELECTRICAL PROPERTIES OF Fe³⁺ DOPED METHACRYLIC ACID – ETHYLACRYLATE (MAA:EA) COPOLYMER ELECTROLYTES

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ABSTRACT

Methacrylic Acid – Ethylacrylate (MAA:EA) copolymer electrolytes doped with different concentration of Fe³⁺ were prepared using the casting technique. Electrical conductivity of the films was measured with impedance analyzer in the frequency range of 1 Hz to 1 MHz and in the temperature range of 303–348 K. It was observed that the magnitude of conductivity increased with the increase in the salt concentration as well as the temperature. UV-Vis. optical absorption spectrum indicates a variation in both intensity and optical energy gap with different concentration of doping level. Both values of direct and indirect energy gaps are calculated and discussed. Obtained data shows a defect formation which increases with increasing Fe³⁺ concentration. This suggests that FeCl₃, as a dopant, is a good choice to improve the electrical properties of MAA:EA copolymer electrolytes.

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INTRODUCTION

Considerable attention has been focused recently on the synthesis of conducting organometallic polymers. One of the most interesting areas of metal-containing polymers is that of electrically conducting organometallic polymers. The most promising conducting polymer should demonstrate good solution or melt processability, in addition to environmental stability, mechanical integrity and controllable conductivities. Because the ability to tailor the electrical properties of these materials is one of the most attractive features and coupled with improved stability and processability relative to the original conducting polymer systems. Applications of these polymers include Remotely Readable Indicators, Biosensors, Storage Battery and Fuel Cell Electrodes, Capacitors, Electrochromics, Chemical and Biochemical Sensors, Ion Exchange release devices and Neutron detection. Methacrylic Acid- Ethyl Acrylate (MAA:EA) copolymer has drawn special attention amongst the copolymers because of its good environmental stability, easy process and transparency. MAA:EA copolymer is a potential material having good charge capacity and dopant dependent electrical and optical properties. Bajaj *et al.* (1994)

studied the thermal behavior of MAA:EA copolymers. Wang *et al.* (2003) studied the interaction between MAA:EA copolymer and bromide dopant. The method of choice for producing conducting organometallic polymers involves complexing transition metals with conjugated bridging ligands. The ability to alter the oxidation state of the metal ion, and thus the charge density along the polymer backbone, provides an alternative route to charge carrier creation as opposed to redox doping. Its electrical conductivity depends on the thermally generated carriers and the addition of suitable dopants (Mehendru *et al.*, 1997; Shinka *et al.*, 1989). Fe³⁺ was selected as an attractive candidate for this doping process because of its interesting physical properties. It should be noted that formation of stable metal particles inside the polymer system is also of interest for potential application such as 3D storage of optical data, shielding of electromagnetic radiation flexible elements for resistive heating (Taufhri *et al.*, 2002; Abdelaziz, 2008), laser systems, optical lenses and integrated wave guides. Based on the importance and relevance of the MAA:EA copolymer as a suitable matrix for transition metal ion such as Fe³⁺ ions, the combined optical, and electrical conductivity investigations of MAA:EA films doped with different concentrations of Fe³⁺ ions represent an important task of this work. Moreover, so far no work was reported on Fe³⁺ ions doped MAA:EA films. Hence, the authors have aim at the present investigation.

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MATERIALS AND METHODS

Methacrylic acid - ethyl acrylate (1:1) dispersion 30 percent copolymer with molecular weight 2,50,000 was purchased from Merck Millipore India Ltd. MAA:EA copolymer films (14 μm thickness) doped with Fe³⁺ in various concentrations were prepared at room temperature by solution casting method. The desired concentrations of FeCl₃ solution (1, 2, 3, 4 and 5 mol%) were prepared by using distilled water. 5ml of MAA:EA copolymer was dissolved in distilled water separately. Different amounts of (1, 2, 3, 4 and 5 mol%) Fe³⁺ ions were added into the copolymer solution. The solution was magnetically stirred for 10-12 hours to get homogeneous mixture and then cast onto plastic dishes. The film was slowly evaporated at room temperature to obtain free standing copolymer film at the bottom of the dishes. UV-Vis absorption spectra of the prepared samples were recorded in the range 200-800 nm at room temperature using JASCO UV-VIS-NIR spectrophotometer (model- V.700). From these data the optical constants such as band edge, optical band gap (both direct and indirect) were determined. The impedance measurements were performed using a computer controlled phase sensitive multimeter (PSM 1700) in the frequency range of 1 Hz–1 MHz and in the temperature range of 303–348 K. The samples were vacuum dried at 313 K for 1 h and the measurements were done by sandwiching the electrolyte film between two aluminum electrodes in a temperature controlled INDFURR furnace.

RESULTS AND DISCUSSION

Impedance analysis

AC impedance spectroscopy has become a powerful tool for the investigation of ionic conductivity of solid electrolyte films. Fig. 3 shows the typical impedance plot of Fe³⁺ doped MAA:EA copolymer (5 mol%) at different temperatures in the frequency range of 1Hz–1MHz below 75 °C. It has been found that the idealized impedance plane plots of Z^{II} as a function of Z^I, i.e. Cole–Cole plots of the films (Z^I and Z^{II} denote the real and imaginary parts of the complex impedance Z*), contain a semi circular arc and inclined spike, which together are characteristic behavior of ionically conducting solids with blocking electrodes (Prabu *et al.*, 2010). The semicircle is due to the parallel combination of bulk resistance (due to the migration of ions) and bulk capacitance (due to the immobile polymer chains). Hence the frequency response of the given sample could be represented by an equivalent circuit consisting of a parallel combination of the circuit elements R (resistance) and C (capacitance). The presence of the depressed semi circle reveals the non-Debye nature of the sample (Lanfredi and Saia, 2002) due to the potential well for each site, through which the ion transport takes place, not being equal. The inclined spike represents formation of double layer capacitance at the electrode–electrolyte interface due to the migration of ions at low frequency. The capacitance values are in the range of pF, which represents the bulk response of the sample (Bohnke *et al.*, 1999). The electrode double layer at each interface possesses increasing impedance against ion transfer with decrease in frequency, which, in the Nyquist plot of impedance spectra, was represented by an inclined spike (Li and Hsu,

1984). Furthermore the inclination of the spike at an angle less than 90 °C to the real axis is due to the roughness of the electrode–electrolyte interface (Ramya *et al.*, 2008).

The ionic conductivity of pure and Fe³⁺ MAA:EA copolymer electrolytes is calculated from the relation

$$\alpha = \frac{l}{R_b A}$$

where *l*, is the thickness of the film, *A*, the area of the film and *R_b*, the bulk resistance of the film material which is obtained from the intercept on the real axis at the high frequency end of the Nyquist plot of complex impedance (Macdonald, 1987).

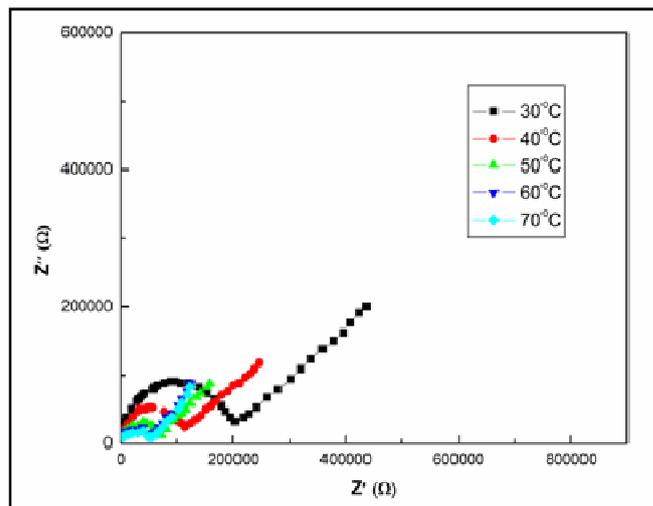


Fig.1. Cole–Cole plots for (MAA:EA/Fe³⁺) (5mol%) copolymer electrolyte at different temperatures

Composition dependence of conductivity

The variation of conductivity (σ), as a function of Fe³⁺ concentration in pure at different temperatures is shown in Fig. 3. From the figure, it is seen that the conductivity of pure MAA:EA is about $8.25 \times 10^{-9} \text{ Scm}^{-1}$ at room temperature and increases to $1.14 \times 10^{-7} \text{ Scm}^{-1}$ for 5 mol% of Fe³⁺ ions. The increase in ionic conductivity with the addition of Fe³⁺ is attributed to a reduction in crystallinity of copolymer electrolyte and also the increase in number of mobile charge carriers. The coordination interactions of the either oxygen atoms of MAA:EA with Fe³⁺ cations, which result in a reduction in crystallinity of MAA:EA copolymer, are responsible for the increase in ionic conductivity. The maximum conductivity shows the maximum and effective interaction between oxygen atoms and Fe³⁺ cations in the electrolytes (Noor *et al.*, 2010). A reduction in crystallinity of MAA:EA electrolytes can also be seen from the XRD analysis that shows a decrement in the intensity of sharp crystalline peaks with the addition of Fe³⁺ ions, which results in a dominant amorphous phase in the electrolytes. A polymer chain in the amorphous phase is more flexible, which results in an increase in segmental motion of the polymer, which facilitates higher ionic mobility (Park *et al.*, 2003). Fe³⁺ ions dissociation is an additional factor in enhancement of ionic conductivity. The dissociation of dopant will promote more

free Fe^{3+} ions transfer into the electrolyte. The increment in conductivity with dopant concentration due to the rise in the number of charge carriers is shown in Fig. 4. The conductivity data of pure and Fe^{3+} doped MAA:EA copolymer at room temperature are presented in Table 1.

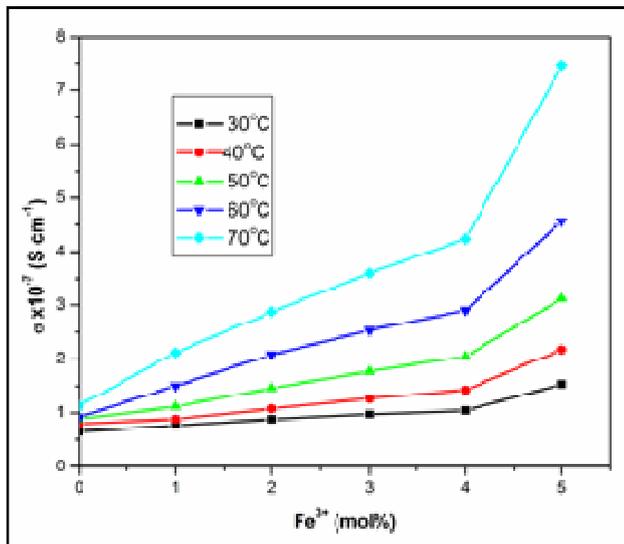


Fig.2. Conductivity vs. dopant concentration plots of (MAA:EA/ Fe^{3+}) copolymer electrolyte system at different temperatures

Temperature dependence of conductivity

The bulk conductivity has been calculated from the impedance plot, and logarithms of conductivity were plotted against the inverse of temperature to observe the temperature dependence of conductivity. Fig.5 shows the linear dependence of $\log \sigma$ on inverse temperature ($1000/T$) for pure and Fe^{3+} doped MAA:EA copolymer films. The linear variation in $\log \sigma$ vs. $1000/T$ plot suggests an Arrhenius-type thermally activated process represented by

$$\sigma_{dc} = \sigma_0 \exp(-E_a / KT)$$

where σ_0 is the pre-exponential factor, E_a the activation energy, k the Boltzmann constant and T the absolute temperature. The magnitude of ionic conductivity was found to increase with increase in temperature in all compositions of the polymer blend electrolyte system including pure film. This may be explained on the basis of an increase in either ionic mobility or the concentration of carrier ions (MacCallum and Vincent, 1987). In polymer electrolytes, change of conductivity with temperature is due to segmental motion, which results in an increase in the free volume of the system (Druger *et al.*, 1985). When temperature is increased, the vibrational energy of a segment is sufficient to push against the hydrostatic pressure imposed by its neighbouring atoms and create a small amount of space surrounding its own volume in which vibrational motion can occur (MacCallum and Vincent, 1987). Therefore, the free volume around the polymer chain causes the mobility of ions and polymer segments and, hence, the conductivity increases. The increase of temperature causes the increase in conductivity due to the increased free volume and their

respective ionic and segmental mobilities. This increase in free volume would facilitate the motion of ionic charges (Park *et al.*, 2003).

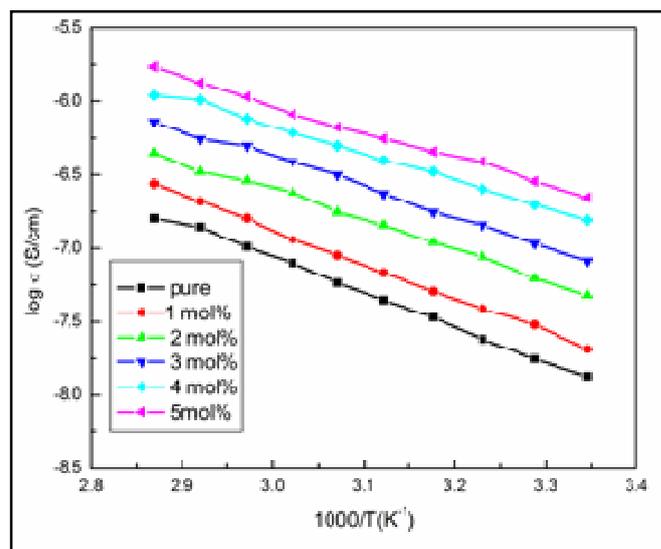


Fig.3. Inverse temperature dependent conductivity of pure MAA:EA and Fe^{3+} doped copolymer electrolyte films of different concentration

Activation energies

The activation energies were calculated from the slope of the Arrhenius plots and the values are shown in Table 1. The activation energy is a combination of energy of charge carrier creation (defect formation) and the energy of ion migration that can be evaluated by linear fitting of the $\log \sigma$ vs $1000/T$ plots (Famiza *et al.*, 2006; Reddy *et al.*, 1999). Therefore, it can be suggested that the activation energy is due to the energy that is required to provide a conductive condition for the migration of ions. From the table it was found that the activation energy values decreased with increasing concentration of Fe^{3+} . This may be due to the fact that the addition of small amounts of dopant forms charge transfer complexes in the host lattice (Rama Mohan *et al.*, 2011). These charge transfer complexes increase the electrical conductivity by providing additional charges in the lattice, resulting in a decrease of activation energy.

Table 1. Conductivity and activation energies of undoped and Fe^{3+} doped MAA:EA copolymer electrolyte films.

Concentration Mol% Fe^{3+} :MAA:EA	Conductivity at 303 K (S/cm)	Activation energy E_a (eV)
Pure	8.25×10^{-9}	0.53
1	3.26×10^{-8}	0.50
2	5.78×10^{-8}	0.48
3	6.25×10^{-8}	0.46
4	0.22×10^{-7}	0.43
5	1.14×10^{-7}	0.41

UV-Vis Absorption studies

Absorption spectroscopy is a technique wherein the absorption of electromagnetic wave is measured as a function of the frequency or wavelength. The absorption process induces an

interaction between electromagnetism and the sample, which can be interpreted through variations in the absorption spectra. An absorption spectrum is a fingerprint of a molecule or polymer material. UV-Vis absorption is a commonly used analytical tool for studying the interactions between electrons and radiation. The absorptions of copolymer electrolytes for pure and Fe³⁺ doped are shown in the Fig. 1. The maximum absorption for all the samples is in the range of 200–800 nm. According to the graph, The doped of Fe³⁺ in MAA:EA introduces a new absorption peak at 284 nm, in addition to the peak at 221 nm characteristic of pure MAA:EA were observed, these new peak may be attributed to the formation of charge transfer complex (Uma Devi *et al.*, 2002). The amount of absorbance at each peak position increasing with dopant concentration, this drop in absorption edge is the result of the decreased band gap which improves the sample semiconducting behaviour.

The absorption coefficient α is directly determined from the spectra by

$$\alpha = \left(\frac{A}{d}\right) 2.303 \quad (2)$$

Where A is the absorbance and d is the thickness of the film. The variation in the absorption coefficient with incident photon energy for undoped as well as doped MAA:EA copolymer (Fig. 2) shows that the absorption edge for undoped MAA:EA lies at 4.97 eV while for doped films the values are found to decrease from 4.88 to 4.55 eV (Table. 2).

When a direct band gap exists, the absorption coefficient has the following dependence on the energy of the incident photon (Davis and Shalliday, 1960; Thutupalli and Tomilin, 1976).

$$\alpha h\nu = c(h\nu - E_g)^{\frac{1}{2}} \quad (3)$$

where E_g is the band gap, c is a constant, ν is the frequency of light and h is the Planck's constant.

A plot of $(\alpha h\nu)^2$ vs $h\nu$ (photon energy) as shown in Fig 3 is observed to be linear. The intercept on the energy axis by extrapolating the linear portion of the curve to zero absorption value may be interpreted as the value of the band gap. For pure (MAA:EA) film, the direct band gap lies at 5.09 eV while for doped films the values vary from 5.05 to 4.79 eV which are given in Table 2. For indirect transition which requires phonon assistance, absorption coefficient has the following dependence on the photon energy (Davis and Shalliday, 1960; Thutupalli and Tomilin, 1976).

$$\alpha h\nu = A(h\nu - E_g + E_p)^2 + B(h\nu - E_g - E_p)^2 \quad (4)$$

Where E_p is the energy of phonon associated with transition and A, B are constants depending on the band structure.

The indirect band gaps were obtained from the plots of $(\alpha h\nu)^{1/2}$ vs $h\nu$ (Fig. 4). For pure (MAA:EA) copolymer film the indirect band gap lies at 4.85 eV, while for doped films the values vary from 4.73 to 4.19 eV (Table 1). From Table 2, it is clear that

the band edge, direct band gap and indirect band gap values showed decrease with the increase of dopants. The decrease in optical band gap on doping may be explained on the basis of the fact that incorporation of small amount of dopants form charge transfer complexes in the host lattice. The band edge, direct band gap and indirect band gap values shifted to lower energies on doping with Fe³⁺ ions, this is due to inter band transitions (Reddeppa *et al.*, 2013).

Table 2. Absorption edge optical band gap values of pure and Fe³⁺ ions doped (MAA:EA) copolymer electrolytes

Concentration Mol% Fe ³⁺ : MAA:EA	Absorption edge (eV)	Direct band gap energy(eV)	Indirect band gap energy(eV)
Pure MAA:EA	4.97	5.09	4.85
1	4.88	5.05	4.73
2	4.80	5.02	4.67
3	4.71	4.90	4.47
4	4.65	4.86	4.33
5	4.55	4.79	4.19

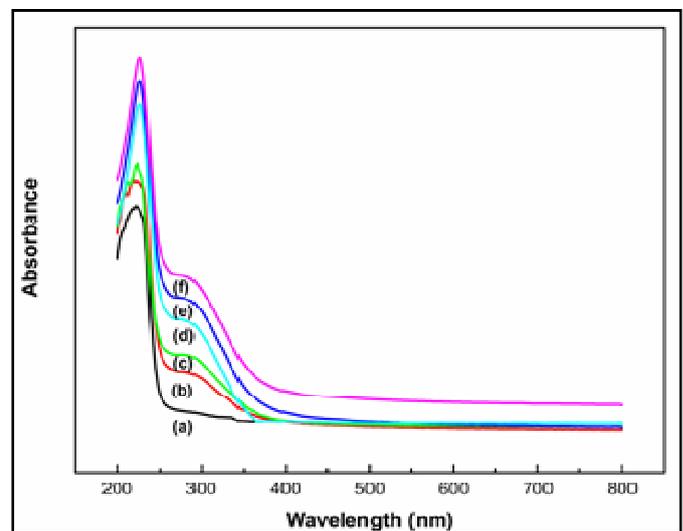


Fig. 4. Ultra Violet absorption spectra for MAA:EA copolymer electrolytes containing Fe³⁺ (a) pure (b) 1 mol% (c) 2 mol% (d) 3 mol%. (e) 4 mol% (f) 5 mol%

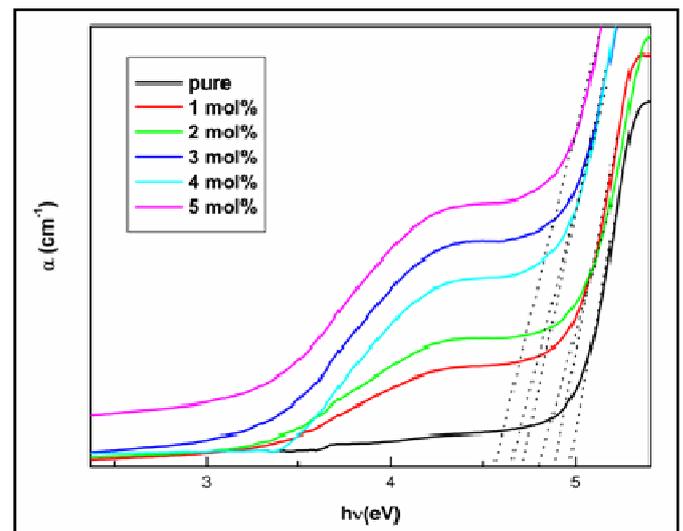


Fig. 5. α vs $h\nu$ plots of pure and a Fe³⁺ doped MAA:EA copolymer electrolytes

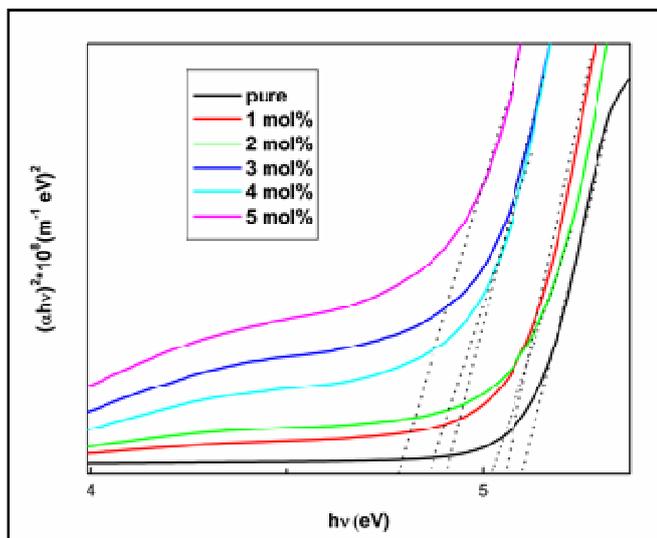


Fig. 6. $(\alpha hv)^2$ vs $h\nu$ plots of pure and Fe^{3+} doped MAA:EA copolymer electrolytes

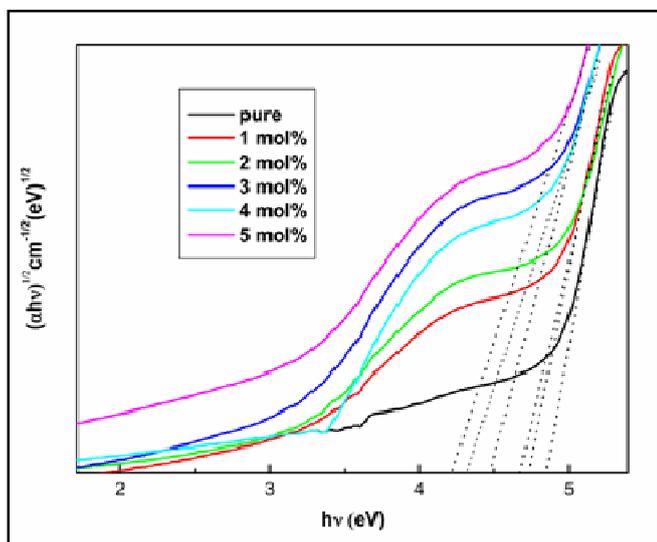


Fig. 7. $(\alpha hv)^{1/2}$ vs $h\nu$ plots of pure and Fe^{3+} doped MAA:EA copolymer electrolytes

Conclusion

Polymer electrolytes based on MAA:EA copolymer with $FeCl_3$ as the dopant at different concentrations were prepared using solution casting technique. The impedance study showed that the addition of Fe^{3+} ions to the polymer electrolyte enhanced the ionic conductivity. The increase in the conductivity with an increase in concentration of Fe^{3+} was attributed to an increase in the amorphosity. Optical absorption edge and optical band gaps (both direct and indirect) showed a decreasing trend with increased concentration of the dopant. These data suggest that the present electrolyte system is a worthy candidate for electrochemical device applications.

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