Supporting Information

Cationic defects engineered $CuMn_2O_4$ photothermal membrane to leverage interfacial solar steam generation

Harshada S. Jadhav,[a,] Ekta Choudhary,[b] Manopriya Samtham,[a] Ajay Patil,[a] Suman Yadav,[a] Sameena R. Mulani,[a] Rajashri Urkude,[c] Ravindra Jangir,[d,e] Parvez A. Shaikh,[f],** and Rupesh S. Devan[a,g,*]

a. Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Indore, Simrol, Khandwa Road, Indore, 453552, India. rupesh@iiti.ac.in
b. Department of Physics, Indian Institute of Technology Indore, Simrol, Khandwa Road, Indore, 453552, India.
c. Beamline Development and Application Section, Bhabha Atomic Research Centre, Mumbai 400085, India.
d. Accelerator Physics and Synchrotrons Utilization Division, Raja Ramanna Centre for Advanced Technology, Indore 452013, India.
e. Homi Bhabha National Institute, Anushakti Nagar, Mumbai 400094, India.
f. Department of Physics, AKI's Poona College of Arts, Science and Commerce, affiliated to Savitribai Phule Pune University, Pune 411001, India. parvezshaikh0@gmail.com
g. Centre for Electric Vehicle & Intelligent Transport System, Indian Institute of Technology Indore, Khandwa Road, Simrol, Indore, 453552, India.

A] Complex Impedance Spectroscopy analysis

Complex Impedance Spectroscopy (CIS) is a very useful tool for studying the electrical properties of materials that exhibit a complex interplay of conductive and insulating behavior, even with very small amount of compositional change. CIS enables the clear separation of bulk (intra-grain) through impedance (Z) formalisms.

The complex impedance Z*(ω) can be defined as:

$$= Z'(\omega) + j\,Z''(\omega) \quad (1)$$

where Z' and Z'' ascribed to the real and imaginary parts of impedance, respectively, are derived as follows:

$$Z' = \frac{R_G}{1 + (\omega R_G C_G)^2} + \frac{R_{GB}}{1 + (\omega R_{GB} C_{GB})^2} \quad (2)$$

and

$$-Z'' = R_G\left(\frac{\omega R_G C_G}{1 + (\omega R_G C_G)^2}\right) + R_G\left(\frac{\omega R_{GB} C_{GB}}{1 + (\omega R_{GB} C_{GB})^2}\right) \quad (3)$$

The shift in frequency peak positions to the higher side with increasing temperature represents the temperature-dependent electrical relaxation phenomena present in the material (Fig. S1). Generally, the activation energy of relaxation phenomena is determined from the Arrhenius Eq. (4),

$$fz''_{max} = B\exp\left(-E_a/K_BT\right) \quad (4)$$

Where, Ea is the activation energy, B is the pre-exponential factor, KB is the Boltzmann constant, and T is the temperature. fz''_{max} is the frequency at which the maxima occur in the Z″. fz''_{max} and T are determined experimentally. E_a is determined by fitting the Arrhenius plot of ln(fz''_{max}) versus $1/K_BT$, as shown in Fig. S1.

Activation energies (E_a) determined from the linear fitting of the Arrhenius plot are 0.129 eV for CMO_{NP} and 0.144 eV for CMO_{NF}. This activation energy is attributed to the charge transfer between Mn^{4+}/Mn^{3+} sites.[1] Change in the E_a value for CMO_{NF} indicates modifications in the defect states, which directly influence charge-transport mechanisms. Since activation energy represents the barrier for carrier movement in the defect-mediated conduction process in metal oxides, this increment suggests altered defect dynamics in CMO_{NF}.

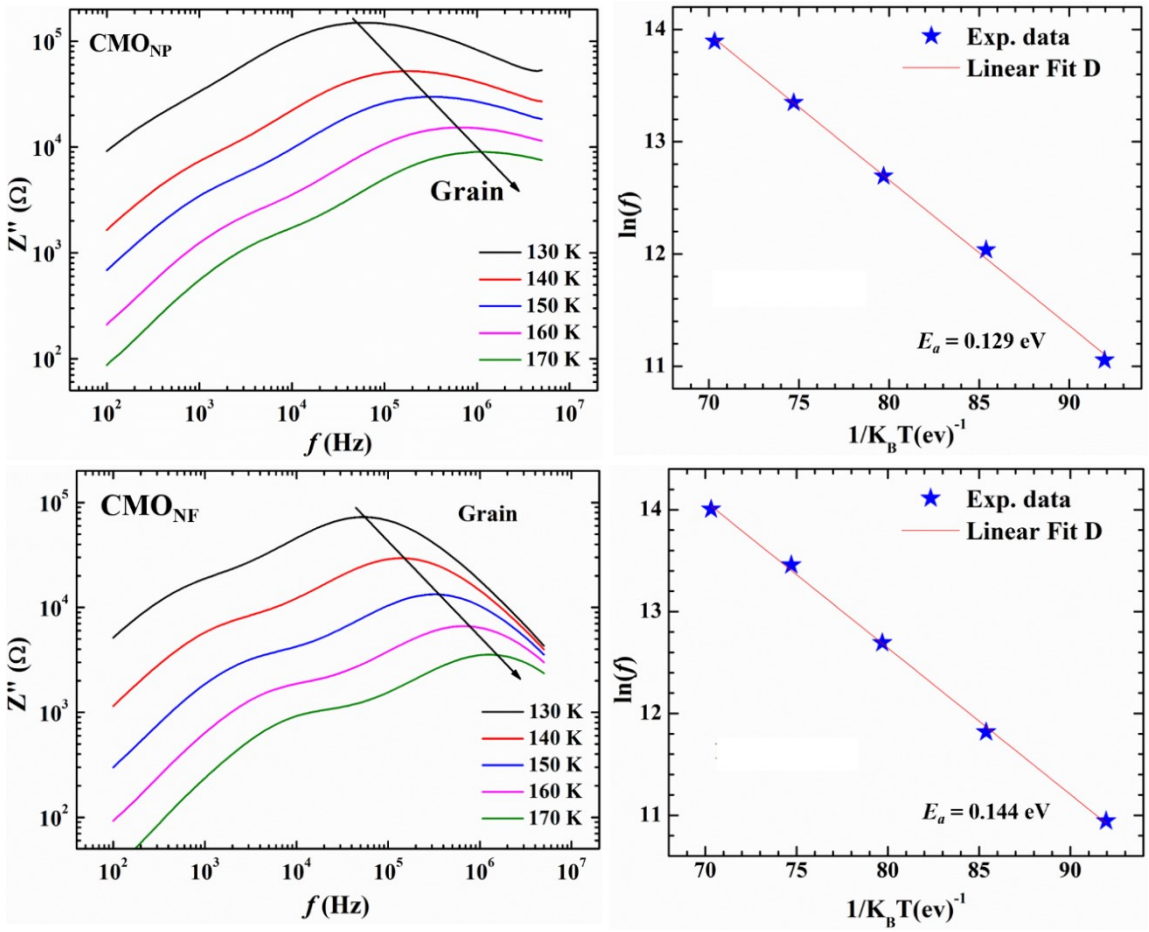

Fig. S1. Frequency-dependent plots of the imaginary part of impedance (Z″) measured at various temperatures and the linearly fitted Arrhenius plots for CMO_{NP} (upper panel) and CMO_{NF} lower panel.

References

[1] A. Leonarska, M. G. Kądziołka, A.Z. Szeremeta, *J. Mater. Sci*.,**2017**, 52, 2222–2231.