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Study of functional properties of some spinel materials as electrodes for Supercapacitor applications

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- Heiba, Z. K., Deyab, M., Mohamed, M. B., **Farag, N. M.**, El-naggar, A., & Plaisier, J. R. (2021). Electrochemical performance of CuCo₂O₄/CuS nanocomposite as a novel electrode material for supercapacitor. *Applied Physics A*, 127(11), 1-10
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- Zein K. Heiba¹, M.A. Deyab, **Noura M. Farag**, Mohamed Bakr Mohamed, Sameh I. Ahmed, Electrochemical performance of nano CuCo₂O₄ and MnS solid solution. *J Sol-Gel Sci Technol* (2022). <https://doi.org/10.1007/s10971-022-05857-2>

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