

A NOVEL CARBONACEOUS COMBUSTION METHOD TO SYNTHESISE LiMeVO₄ COMPOUNDS (Me = Mn, Co)

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Following the discovery of LiNiVO₄ by Fey et al.¹, the possibility of using LiMeVO₄ compounds (Me=Mn, Co & Fe) as cathodes for li-batteries has been thought of with varied interests². The electrochemical activity of LiMnVO₄ (orthorhombic spinel) and the structural arrangement of LiCoVO₄ (inverse spinel) are the prime factors that are intriguing to study the role and the arrangement of transition metal atoms in these vanadates. A new concept of using a carbonaceous compound viz. gelatin as the combustible component has been introduced in the present study to synthesise LiMnVO₄ and LiCoVO₄ compounds at a temperature as low as 400°C.

Stoichiometric amounts of nitrates of lithium and Mn/Co were mixed with NH₄VO₃ in the form of solution. Gelatin was added to the above solution and heated to 110°C to get a viscous mass which on further heating to 400°C for 3 h resulted in the formation of fine powders of respective vanadates. TG/DTA analysis (Fig.1) is in favour of the initiation of reaction between the reactants and the crystallisation of the products around 300°C itself. The spinel structure of LiMnVO₄ (a = 5.73 & c = 6.31Å) and the inverse spinel structure of LiCoVO₄ (a = 8.18 and c = 8.26Å) are substantiated using XRD results (Fig.2). FTIR peaks corresponding to ν (Li-O-Mn) stretching (640 cm⁻¹) and ν (Li-O-Co) stretching (625 cm⁻¹) and the antisymmetrical ν (VO₄) vibrations (810 cm⁻¹) were observed duely. Presenece of sub-micron sized particles (2 μm) and the uniform distribution of the size reduced particles (1.2 μm) are obvious from SEM and particle size analyses. The discharge profile of both the vanadates (LiMnVO₄ and LiCoVO₄) follow a steadily decreasing voltage characteristics. Cyclic reversibility of the cathodes are established from CV studies (Fig. 3).

References

1. G.T.K.Fey, J.R.Dahn, M.J.Zhang, W.Li, *J.Power Sources*, **68**, 547 (1997).
2. M.Sato, S.Kano, S.Tamaki, S.Misawa, Y.Shirkawa, M.Ohashi, *J. Mater. Chem.*, **6**(7), 1191 (1996).

Fig.1: TG/DTA of LiMnVO₄

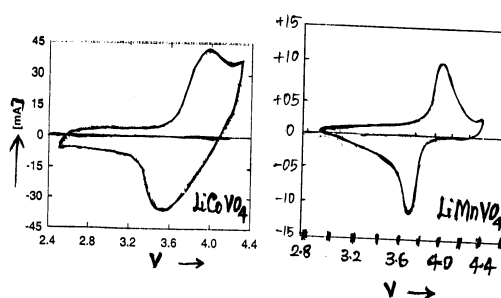
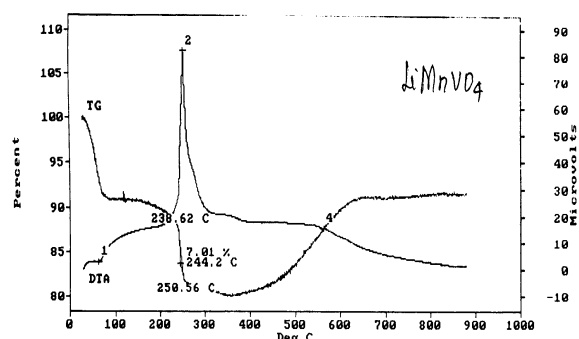


Fig.3: Cyclic voltammogram exhibited by LiCoVO₄ & LiMnVO₄

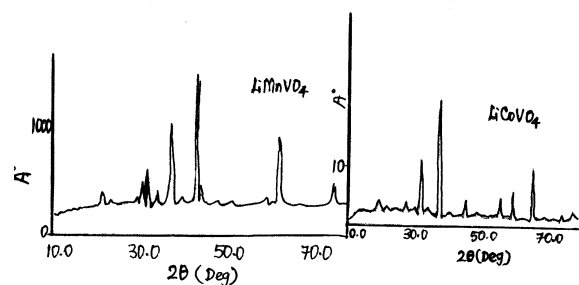


Fig.2 XRD pattern observed for LiMnVO₄ & LiCoVO₄

