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Crystal chemistry of Na insertion/deinsertion in $FePO_4/NaFePO_4$

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Experimental information

C-$FePO_4$ materials were prepared by chemical delithiation of a commercially available carbon coated $LiFePO_4$ (Advanced Lithium Electrochemistry Co.). The chemical oxidation was performed by stirring a mixture of pristine $LiFePO_4$ using NO_2BF_4 (Sigma-Aldrich) as oxidizing agent in acetonitrile (Sigma-Aldrich) at room temperature. The reaction was carried out in a glove box under argon atmosphere (0_2 and H_2O ppm ≤ 5). After the reaction was completed the mixture was vacuum filtered and the delithiated collected powder washed with acetonitrile twice and dried under vacuum at 80 °C overnight. The obtained $FePO_4$ powder was chemically sodiated with NaI (Sigma-Aldrich) in acetonitrile under reflux in argon atmosphere.

The structure and microstructure of the electrode/active materials have been characterized by X-ray diffraction with a Bruker D8 Advance diffractometer and electron diffraction with a FEI Tecnai G2 electron microscope. The composition of the intermediate sample was determined by EDX analysis using a Quanta 250FEG SEM operated at 30kV and equipped with an Apollo 10 SSD EDX detector. The Na/Fe ratio was found to be 0.73 and the 2Na/(Fe+P) ratio 0.72.

Electrochemical measurements were performed in 2-electrode configuration using swagelok type electrochemical cells. The composition of the laminated electrode was: 80 % wt. active material; 10 % wt. binder (PVDF P-5130,Solvay) and 10% carbon black (Super C65,Timcal) with an average loading of 3mg cm^{-2}. High purity metallic sodium was used as the counter electrode and $NaClO_4$ 1M in EC/PC 50-50 wt% mixture as the electrolyte. The cells were galvanostatically cycled in a voltage window of 2-4V vs Na^+/Na.

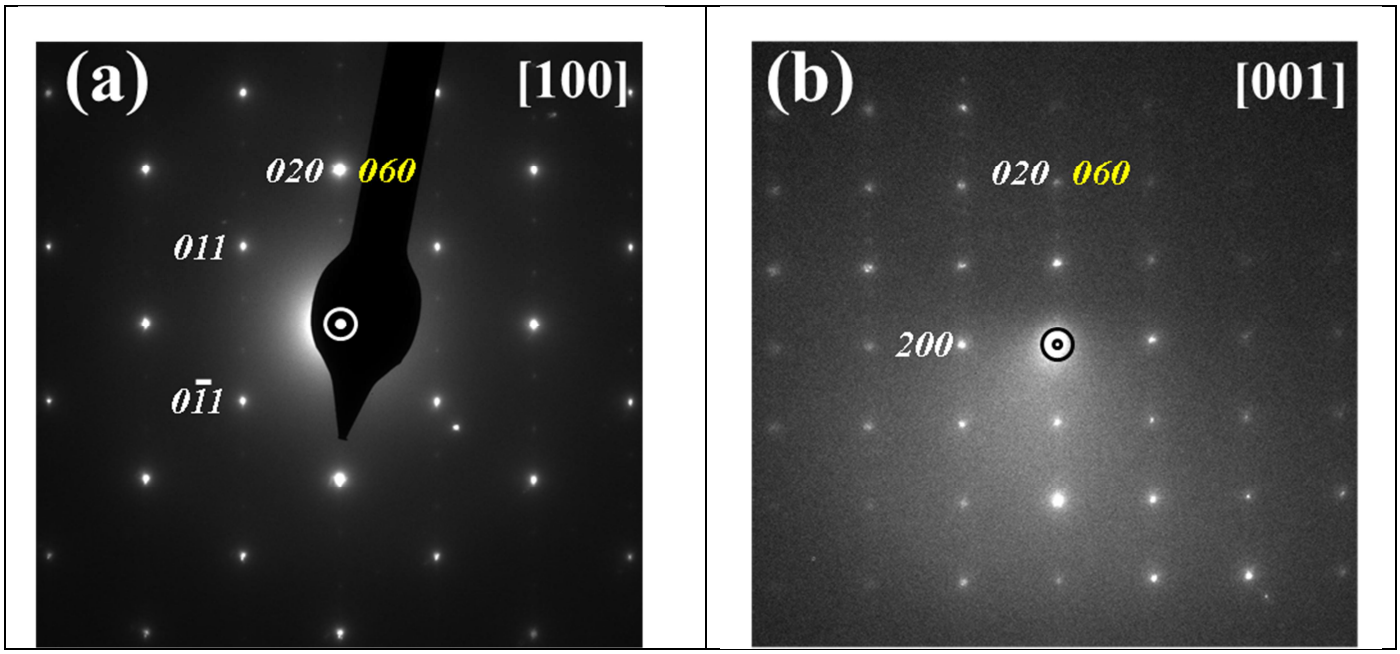

Figure 1: Electron diffraction patterns of $Na_{1-x}FePO_4$ sample corresponding to an a3bc unit cell a) [100] zone axis and b) [001] zone axis.

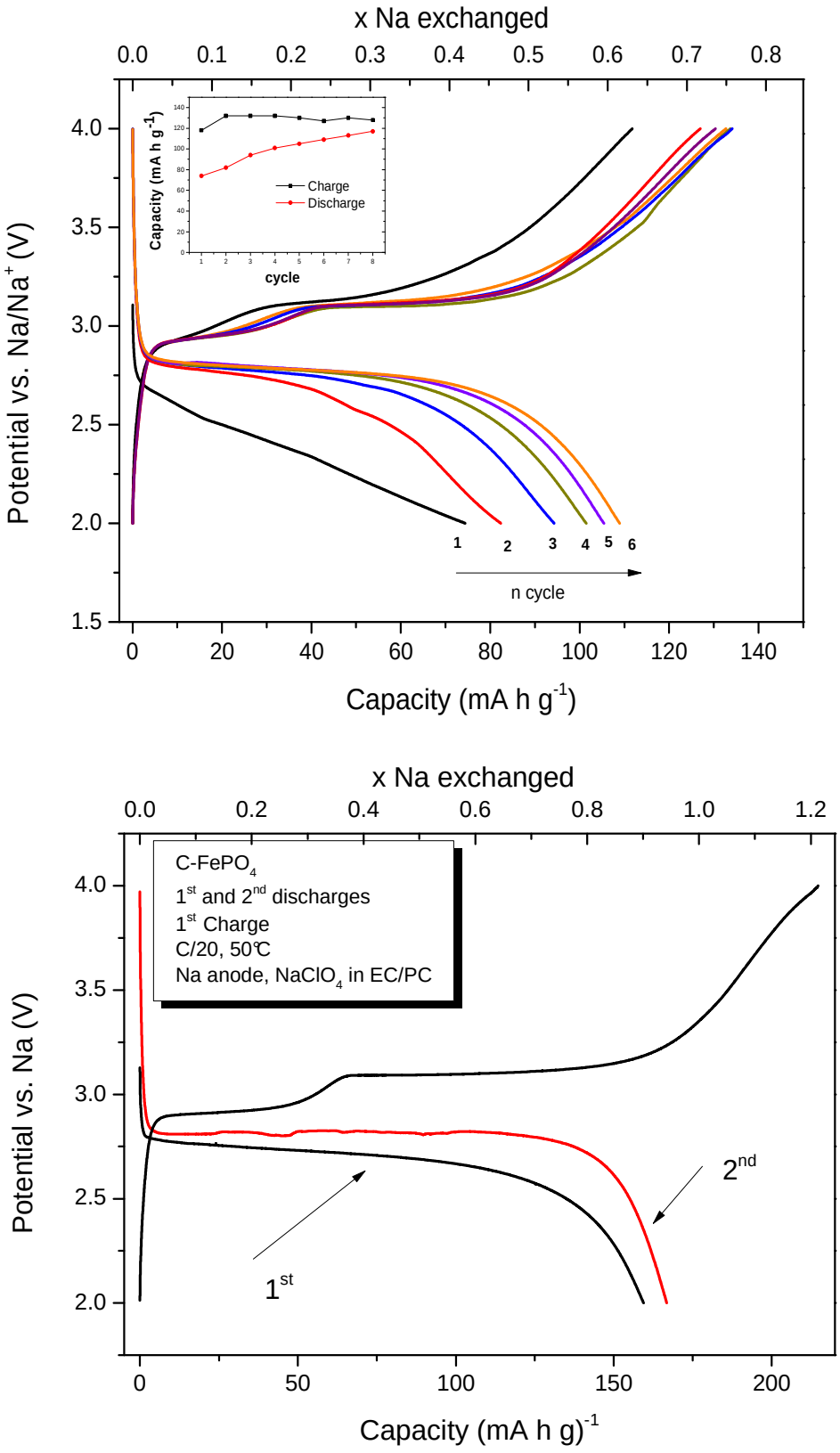

Figure 2: Galvanostatic Na^+ insertion into $FePO_4$ at constant charge and discharge current (C/20) at room temperature (top) and 50°C (bottom). Inset top figure: capacity variation vs. cycle number.