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Magnesium hydride-added titania anode for Li-ion battery

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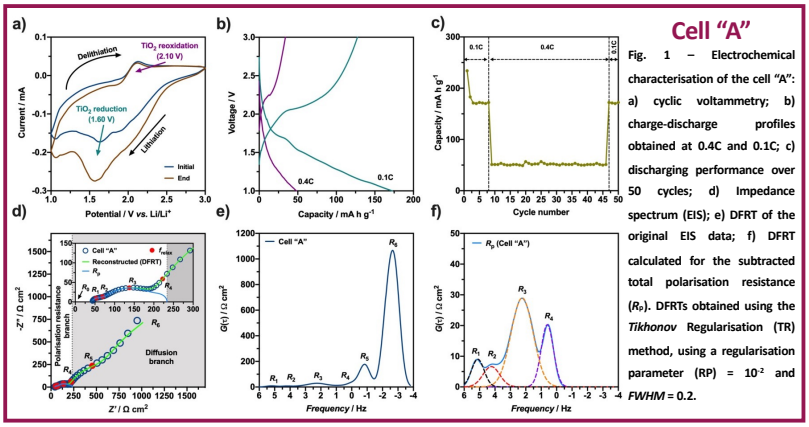
Abstract

Lithium-ion batteries (LIBs) have emerged as the primary choice for portable devices and electric vehicles due to their long-life cycle, high energy density, reasonable production cost, and device design flexibility. This work explores the electrochemical performance of a 10 wt.% MgH_2-added titania anode for Li-ion half-cell batteries. We used a distribution function of relaxation times (DFRT) analysis for quantifying the sources of polarisation losses from the impedance data. We observed a notable increase in both ohmic and polarisation resistance terms for the TiO_2+10 wt.% MgH_2 (**Cell "B"**) compared to the standard titania anode (**Cell "A"**). Moreover, the modified electrode shows a higher lithium diffusion coefficient than pure TiO_2, with capacity retention reaching 300 mA h g^{-1} at 0.1C. After charge/discharge cycles, the formation of a Li-incorporated crystalline structure is revealed in the case of a neat TiO_2 anode. Simultaneously, considerable changes in the crystallinity and microstructure are shown upon lithium insertion for MgH_2 added titania. Atomic Force Microscopy (AFM) studies suggest that a significant morphological evolution occurs upon operation.

Main results

Electrochemical characterisation (Electrochemical Impedance Spectroscopy, EIS; Cyclic voltammetry, CV; Charge-discharge)

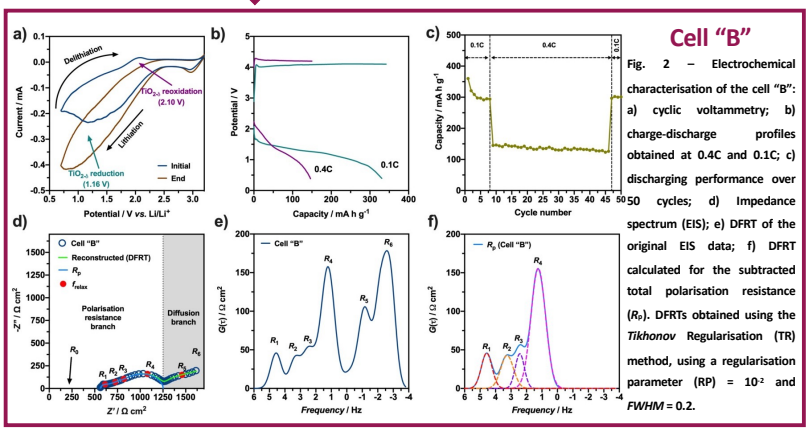


Cell "A"

Fig. 1 – Electrochemical characterisation of the cell "A": a) cyclic voltammetry; b) charge-discharge profiles obtained at 0.4C and 0.1C; c) discharging performance over 50 cycles; d) Impedance spectrum (EIS); e) DFRT of the original EIS data; f) DFRT calculated for the subtracted total polarisation resistance (R_p). DFRTs obtained using the *Tikhonov* Regularisation (TR) method, using a regularisation parameter (RP) = 10^{-2} and *FWHM* = 0.2.

Improved capacity retention from 150 to ~ 300 mA h g^{-1}!

- On the other hand, the charging requires a significantly higher overpotential, with a notable overshooting!
- Notable increase in the charge-transfer processes resistivity



Cell "B"

Fig. 2 – Electrochemical characterisation of the cell "B": a) cyclic voltammetry; b) charge-discharge profiles obtained at 0.4C and 0.1C; c) discharging performance over 50 cycles; d) Impedance spectrum (EIS); e) DFRT of the original EIS data; f) DFRT calculated for the subtracted total polarisation resistance (R_p). DFRTs obtained using the *Tikhonov* Regularisation (TR) method, using a regularisation parameter (RP) = 10^{-2} and *FWHM* = 0.2.

Notable decrease in the diffusion processes resistance!

Table 1 – *Warburg* coefficient (σ) and Li^+ diffusion coefficient (D_{Li^+}) determined for both cells "A" and "B".

Composition	σ / Ω $s^{-0.5}$	D_{Li^+} / cm^2 s^{-1}
TiO_2	158.22	3.59 x 10^{-14}
$TiO_{2-\delta}$	77.66	1.49 x 10^{-13}

Surface characterisation (Atomic force microscopy, AFM)

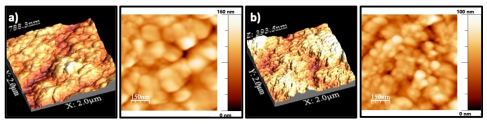


Fig. 3 – Typical topographic images obtained by AFM for of the as-prepared a) Cell "A" and b) Cell "B" anodes.

Both the grain size (from 100 nm to < 50 nm) and the surface roughness (root mean square, RMS) (from 117 to 65 nm) have decreased with the addition of MgH_2.

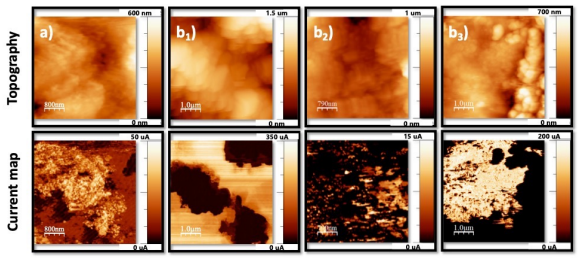


Fig. 4 – Surface topographic and current maps (+0.5 V) obtained by AFM for the anode samples: a) Cell "A"; b_1) as prepared Cell "B"; b_2) cycle #2 "Cell "B"; and b_3) cycle #20 Cell "B".

- The Cell "A" shows a reasonably better current distribution than in Cell "B", implying that the electronic conductivity of samples used in Cell "A" is much better than in Cell "B".
- The overpotential and the overshooting observed in Cell "B" may be due to the lower electronic conductivity of the MgH_2-added titania sample.

Conclusions

A 10 wt.% MgH_2-added titania and neat titania additives were tested as anodes for CR2032 model Li-ion half cell batteries. Better capacity retention was observed in the former case (~ 300 mA h g^{-1}), as compared to the latter case (~ 170 mA h g-1). The charging-discharging studies demonstrate notable differences between the neat TiO_2 and MgH_2-added TiO_2. Despite higher charge-transfer resistivity, the MgH_2-added titania facilitates higher diffusion of Li^+, which may be due to the influence of lattice nonstoichiometry. These observations are further supported by the AFM observations.

Acknowledgements

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