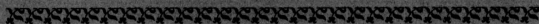
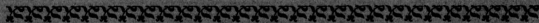


CHAPTER

5



ELECTROCHEMICAL CELL ANALYSIS



5.1 The Li/AC+EC+LiCF₃SO₃/V₂O₅ cell

A schematic representation of the Li/AC+EC+LiCF₃SO₃/V₂O₅ cell is as shown in Fig. 5.1.

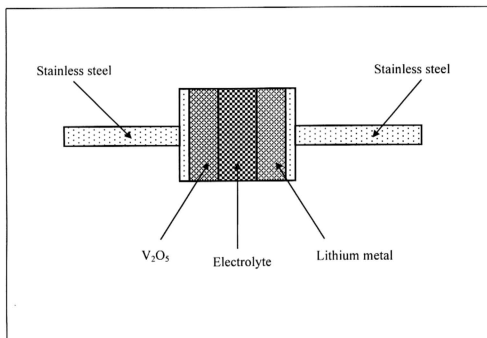
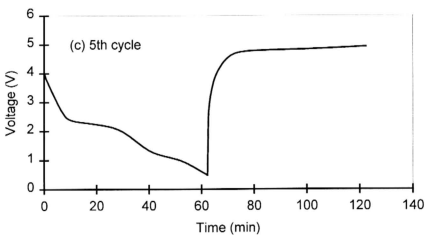
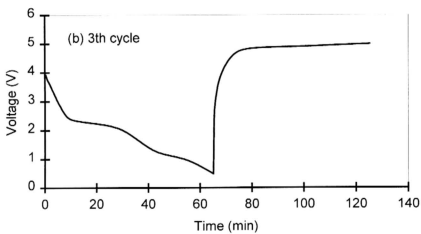
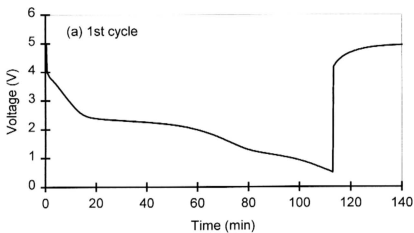


Fig. 5.1: Schematic representation of fabricated cell.

Several charge/discharge currents were tried by trial and error and finally upon charging the cell with a current of 100 nA and discharging it at 10 nA a reasonable discharge characteristic was obtained for study that could last for as long as 10 cycles.

Fig. 5.2 shows the discharging and charging profile of the electrochemical cell that was fabricated. From the discharging characteristics, it can be observed that the internal resistance of the cell is very high. The internal resistance is estimated to be $10^8 \Omega$ whereas the resistance of the electrolyte is less than 100Ω . The additional resistance which is parasitic to the cell performance can be attributed to interfacial resistance between the electrolyte and the electrode [83]. Fauteux [84] has also addressed the instability of the electrode-electrolyte contact which affects the cell performance. Hence, in order to improve the performance of this cell, the fabrication technique must be improved so as to achieve a comparable current drain of $>500 \mu\text{A}/\text{cm}^2$ as reported by Iwamoto et al [85]. The internal resistance can be observed to increase with every cycle. During the first discharging cycle, the voltage of the cell dropped to 0.5 V in about 115 minutes. But after the third cycle the cell achieved 0.5 V after about 65 minutes. This cut-off voltage time discharging finally decreased to ~ 50 minutes after the tenth cycle.



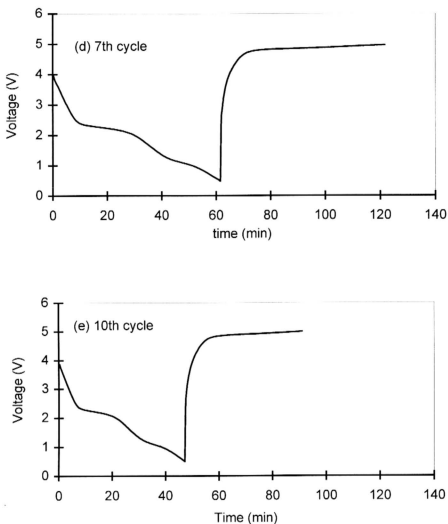
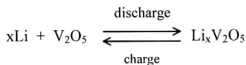


Fig.5.2: Discharge-charge profiles of the (a) first cycle (b) third cycle (c) fifth cycle (d) seventh cycle and (e) tenth cycle

While the cell is undergoing the process of charging and discharging, the polymer is being penetrated by lithium ions. Since the fabricated cell is $\text{Li}/\text{V}_2\text{O}_5$ type, the charge-discharge reaction occurs [86] as follows



This reaction is able to occur because V_2O_5 can intercalate metal ions between the layers of their two-dimensional structure[87] and it is now known that [88] up to 1 lithium per V_2O_5 can be reversibly and easily intercalated. The intercalation reaction is controlled by the diffusion of Li^+ ions through the electrolyte and that is why the electrolyte must show a high permittivity to the lithium ions by having a high electrical conductivity.

Table 5.1 lists several characteristics of the Li/V_2O_5 cell and Fig. 5.3 illustrated how discharge capacity varies with the number of cycles. It can be seen that the discharge capacity for the first cycle is 6.5 nAh. The discharge capacity decreases to 2.5 nAh after the tenth cycle. At the tenth cycle the percentage loss of discharge capacity is 61.5%. Similar problems as encountered in this work has been addressed by Capuano et al [89] and Gummow et al [90]. Capuano et al [89] mentioned that this effect may be associated to the growth of lithium microdendrites across the cell. Furthermore Abraham and Alamgir [91] and Barker et al [92] said that during repeated charging of the cell, dendritic lithium forms on the anode and finally grows through the electrolyte and come in contact with the cathode to create a high impedance or self short. This phenomena was also observed by Inshikawa et al [93] using impedance spectroscopy. The appearance of additional arc response on the semicircle, implies the formation of an additional film on the electrode surface. The uneven deposition of lithium which increases the surface area of the electrode with cycling therefore increases the interfacial resistance. Even if

the electrolyte thickness is reduced to improve ionic transport, the cell resistance will not show an equivalent decrease in resistivity. This is because the interfacial resistances are independent of the polymer electrolyte thickness but dependent on surface contact area [94]. Contact problem is a major problem encountered in this work because the absence of proper electrode-electrolyte contact does not allow the cell to sustain the voltage upon discharging. The formation of lithium dendrites is not only disastrous to the energy density and the cell life, but also severely reduces the cell's safety attributes [94].

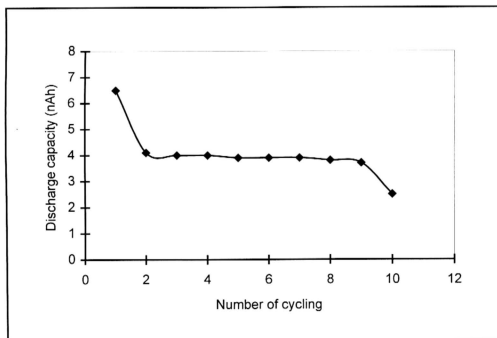


Fig. 5.3: Discharge capacity versus number of cycling of cell $\text{Li}/\text{V}_2\text{O}_5$

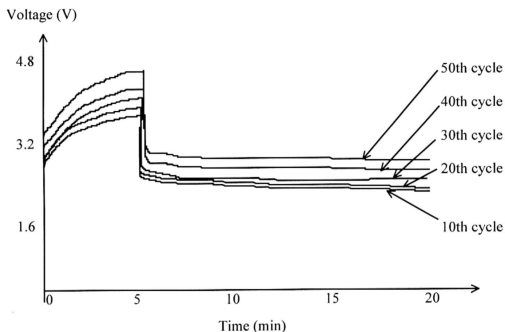
Table 5.1: Characteristics of the cell $\text{Li}/\text{V}_2\text{O}_5$

Number of cycle	Plateau voltage/V	Plateau time/h	Discharge capacity/nAh	Loss of discharge capacity/%
1	2.25	0.65	6.5	-
2	2.25	0.41	4.1	36.9
3	2.25	0.40	4.0	38.5
4	2.25	0.39	4.0	40.0
5	2.25	0.39	3.9	40.0
6	2.25	0.39	3.9	40.0
7	2.25	0.39	3.9	40.0
8	2.25	0.38	3.8	41.5
9	2.20	0.37	3.7	43.1
10	2.17	0.25	2.5	61.5

5.2 The $\text{LiCoO}_2/\text{AC} + \text{EC} + \text{LiCF}_3\text{SO}_3/\text{V}_2\text{O}_5$ cell

In an attempt to improve the cell performance, the lithium metal was replaced with LiCoO_2 and the $\text{LiCoO}_2/\text{AC} + \text{EC} + \text{LiCF}_3\text{SO}_3/\text{V}_2\text{O}_5$ cell was fabricated. After several unsuccessful attempts, we were finally able to charge this cell at $50 \mu\text{A}$ and discharge it at $35 \mu\text{A}$. It seems that the cell can now deliver a higher current. This cell too was charged for 5 minutes but the discharge time was only set for 15 minutes. The cell was operated for 100 cycles. Upon charging the cell has a capacity of $\sim 4000 \text{ nAh}$. The internal resistance of this cell is $\approx 20 \text{ k}\Omega$. Electrolyte-electrode contact is again an

important factor to consider in improving the performance of the cell. Fig. 5.4 shows the charge-discharge characteristics for several cycles. It can be observed from Fig. 5.4 that the cell is more stable and that the drop in voltage is less than 1 volt upon discharge. However this situation can be further improved.



The use of LiCoO_2 makes cell fabrication much easier. It should be noted that vanadium pentoxide is used here as the anode to accept lithium ions from lithium cobaltous oxide during charge and to release them during discharge according to the process:

