

New Advances in Lithium Ion Battery Monitoring

Jörn Tinnemeyer

Vice President - Research & Development
Cadex Electronics Inc.

22000 Fraserwood Way, Richmond BC, Canada V6W 1J6
Joern.Tinnemeyer@cadex.com or www.cadex.com

Abstract: *In the last decade, lithium ion batteries have dominated the market place: first being used in portable consumer products, and now in more industrial and transport-based applications. One necessary requirement of lithium ion batteries -- irrespective of the particular application of interest -- is to gauge how much energy the battery contains and how long a given application can run before the battery needs to be recharged. The precise monitoring and management of lithium ion batteries has proven to be difficult to achieve, especially as the battery starts to age. Here, I describe a novel patented approach that Cadex Electronics Inc., is developing, which assesses the state of charge and state of health of lithium ion batteries by directly measuring the concentration of lithium ions across different states of charge. Directly assessing the electrochemical state of the battery assures very precise monitoring -- conservatively speaking, +/- 5% accuracy, irrespective of which lithium ion chemistries are tested.*

Keywords: state of charge; lithium ion; magnetic susceptibility, magnetic field measurements

Introduction

In our portable world, we use batteries to keep our electronic devices functioning and we monitor the state of the battery to assure that the equipment will operate as we expect. Over the last decade, the applications that use lithium ion batteries have diversified dramatically. Initially, lithium ion batteries (for the remainder of this paper, I will refer to these as Li-ion batteries) were used as the primary power source in electronic devices that benefited from light and powerful batteries -- such as laptop computers and cellular phones. Now, Li-ion batteries are used in a gamut of different electronic technologies, from power tools to transport vehicles. This exponentiating presence of Li-ion batteries in the marketplace makes sense because they effectively store energy (high energy, low weight) with no memory effect, they are cheap to produce, and they are consumable (i.e., possess a limited lifespan), which benefits the retailers through the sale of replacement batteries or new technological devices (Scuilla 2007, Whittingham 2004).

Importantly, though, the praises of Li-ion batteries must be tempered by several key disadvantages in using this chemistry. Namely, they safely operate within a very limited range of conditions; that is, the manufacturers of Li-ion battery packs must be vigilant when developing the protection circuitry and a safe milieu for the battery (McDowall et al., 2007, Van Schalkwijk et al., 2002).

The precise monitoring and management of Li-ion batteries also presents a noteworthy problem -- this problem being the focus of this article. Irrespective of the application being considered, the end-user needs to know when the battery is fully charged and when the battery will run out of power. Intuitively speaking, everyone who uses cellular phones, laptops, or MP3 players knows that predicting when a battery will run out of charge can be elusive, especially as the battery gets older. Within the field of battery management and monitoring, several techniques have been developed that monitor the state of charge of Li-ion batteries and new techniques are up-and-coming. Importantly though, not all techniques are equivalent in their precision or ability to monitor different Li-ion chemistries. Owing to the fundamental role of battery chemistry, I begin this article by providing a brief review of Li-ion chemistries and construction (see also Aurbrach et al., 2007, McDowall 2008, Van Schalkwijk 2002, Whittingham 2004), then I review the advantages and disadvantages of current techniques, and I describe a patented technology that Cadex Electronics is developing that offers the same advantages, without sharing the disadvantages.

Lithium Ion Construction and Consequences for Battery Management

Li-ion batteries are not uniform in construction, rather they may be better characterized as a family of batteries, each possessing its own unique characteristics. Li-ion batteries differ in two fundamental ways -- chemistry and construction.

The name of a particular Li-ion battery is derived from the substances from which it is made, such as 'lithium manganese', 'lithium cobalt', and 'lithium iron

phosphate' batteries (see Table 1). For most Li-ion batteries, the cathode contains the unique chemistries. For example, lithium manganese oxide (LiMn_2O_4) is the cathode material used in lithium manganese batteries, whereas lithium cobalt oxide (LiCoO_2) is the cathode material used in lithium cobalt batteries. The anode materials tend to be more conserved across different Li-ion batteries. Most often, layered carbon (graphite) is used to construct the anode.

Full name	Chemical definition	Abbrev.	Short form	Note
Lithium Cobalt Oxide	LiCoO_2 (60% Co)	LCO	Li-cobalt	Cell phone, laptop, camera
Lithium Manganese (IV) Oxide ¹	LiMn_2O_4	LMO	Li-manganese, also spinel	Power tools, e-bikes, EV, medical, hobbyist
Lithium Iron Phosphate	LiFePO_4	LFP	Li-phosphate	
Lithium Nickel Manganese Cobalt Oxide	LiNiMnCoO_2 (10-20% Co) ¹	NMC	NMC	
Lithium Nickel Cobalt Aluminum Oxide	LiNiCoAlO_2 (9% Co)	NCA	NCA	In development, less commonly used
Lithium Titanate	$\text{Li}_5\text{Ti}_5\text{O}_{13}$	LTO	Li-titanate	

1. $\text{Li}[\text{Ni}_x\text{Mn}_x\text{Co}_{1-2x}]\text{O}_2$ is a more accurate description of NCA, where x is typically 1/3

Table 1 - Examples of lithium ion battery chemistries

These differences in chemistry assure that many simple, generalized attempts to monitor and manage Li-ion batteries are less than ideal (see more below). Indeed, the difficulty in effectively monitoring some of the unique chemistries (e.g., lithium iron phosphate, and lithium nickel manganese cobalt oxide) have thwarted their use in the marketplace, even though these chemistries are, otherwise, very powerful (Deutsche Bank, 2009). That said, Li-ion batteries function in a similar way despite these differences in chemistry. Figure 1 highlights this similarity in function: the lithium ions shuttle between the anode electrode and cathode electrode as the cell charges and discharges, respectively.

Li-ion batteries also differ in their construction. For the purposes of battery monitoring and management, the different forms of cell construction also limit the efficacy of generalized algorithms. Two types of battery cell construction are most common: prismatic cells (Fig. 2 left) and polymer (or pouch) cells (Fig. 2 right). Prismatic cells have an outer metal casing that adds weight and durability to the battery's construction, whereas polymer cells are light-weight and flexible (Tarascon et al., 2001).

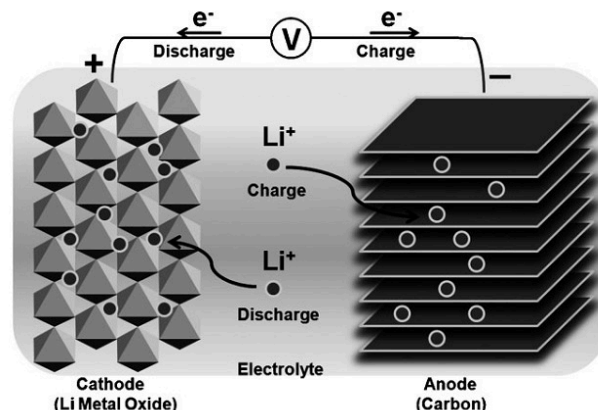


Figure 1 - Lithium ion transport between anode and cathode (Teki et al., 2009)

Moreover, these differences in construction play a vital role in the diffusion characteristics of the lithium ions. Figure 3 illustrates the impedance spectroscopy curves for both the prismatic and polymer designs.

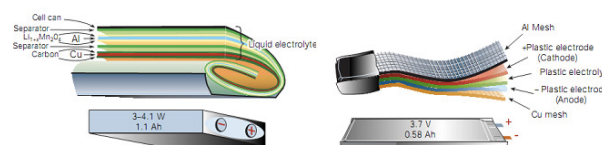


Figure 2 - Prismatic (left) and polymer (right) constructions of lithium ion batteries.

As stated above, differences in chemistry and construction have noteworthy consequences for the different techniques that monitor and manage Li-ion batteries, insofar that they thwart generalized battery management and monitoring solutions. Consider voltage measurements. Voltage measurements have been used for decades as a simple means to monitor and manage Li-ion batteries (and preceding rechargeable battery chemistries). Be that as it may, voltage measurements fall flat for some particular types of Li-ion batteries. For example, the relatively constant voltage output of lithium iron phosphate batteries makes this chemistry resistant to useful voltage measurements when determining state of charge. In the following sections, I highlight many of the different techniques that are currently employed, and a novel patented technique that Cadex Electronics is developing that monitors and manages all Li-ion batteries.

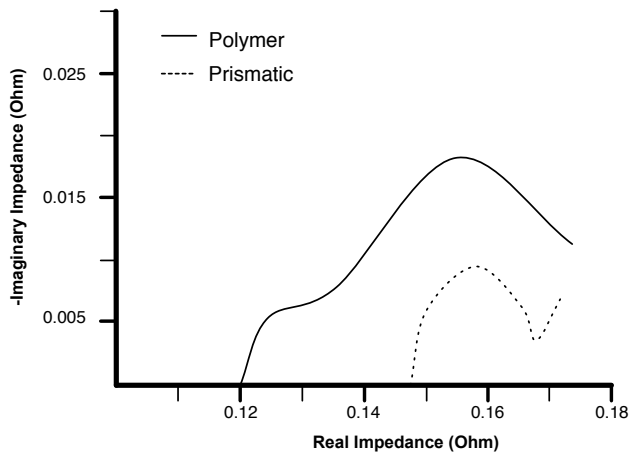


Figure 3 - Impedance spectroscopy differences between prismatic and polymer constructions

Fuel Gauges: State of Charge vs. State of Health

A fundamental task of a battery management system is to report how much energy remains in the battery (how much time the user can expect the application to continue operating). Such *fuel gauges* calculate the *state of charge* of the battery -- the ratio of remaining energy in the battery. The total amount of energy that the battery can possibly hold is called the *state of health*. Both state of charge and state of health are highly dynamic and interdependent. With respect to their dynamic nature, state of charge is modified by polarization currents, whereas the state of health decreases (significantly) as the age of the battery increases. With regards to their interdependence, without knowing state of health, it is impossible to know state of charge because the maximal amount of energy the battery contains (i.e., state of health) is part of the ratio that determines state of charge.

Voltage and the Electromotive Force Curve

Voltage was the first technique that was implemented to monitor and manage battery systems (Buchmann, 2001), and it is one that is still in use today. The battery's voltage originates from the half reactions of each electrode, which in turn depends on the composition of the electrodes. For Li-ion batteries, this has two consequences. First, as the cathode material changes in its composition, the battery voltages change also. Second, as the battery discharges (or charges), the composition of the electrodes change, which, again, leads to changes in voltage. For both reasons, the battery must rest -- stand without any current polarization -- for at least 30 minutes before an accurate measure of voltage can be obtained.

The voltage-based fuel gauge is constructed by measuring the voltage of the battery across different states of charge and then generating an *electromotive force curve* (EMF curve), which estimates the residual energy contained within the battery.

This method, albeit being simple to implement and possessing strong intuitive appeal, has several shortcomings. Consider Figure 4. The solid line illustrates the EMF curve of a battery that is in perfect state of health (a brand new battery). The dashed line illustrates the EMF curve of a battery that is in a 70% state of health (an old battery at a state, in which battery monitoring is notoriously difficult). Importantly, the lines do not overlap perfectly; therefore, the same curve may not be used as the battery ages.

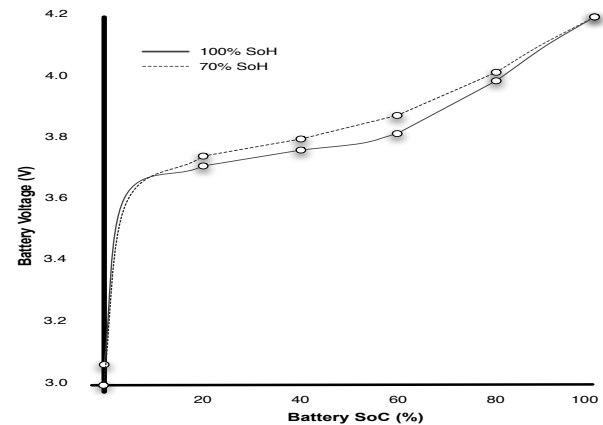


Figure 4 EMF curves for two batteries at different states of health

This shortcoming of voltage measurements has long been identified (Pop et al., 2007). To compensate for this problem, mathematical aging models have been developed to account for the age of the battery. However, even with the mathematical models implemented, voltage measurements are imprecise -- more than +/-10% divergences have been reported (Pop et al., 2007).

Another problem when using voltage measurements and EMF curves is the amount of time the user must wait before the reading is meaningful (i.e., before the voltage asymptotes). For most batteries, at least 30-60 minutes must elapse before the EMF curve accurately estimates state of charge (Coleman et al., 2007). For most users, this timeframe is impractical. Indeed, if there is *any* current draw (polarization) or if the voltage is monitored shortly after a polarization event, the voltage reading is incorrect. Once again, mathematical models are used to correct for this shortcoming, but the models must consider

scores of conditions; as such, one model cannot effectively manage all situations and/or all applications.

Figure 5 illustrates a much more significant problem in using voltage measurements and EMF curve estimations -- the inability to generalize this technique across different Li-ion chemistries. This graph plots the difference between the battery's state of charge and its voltage. As illustrated with the solid line, lithium cobalt batteries yield a clear stepwise trend across state of charge -- the higher the state of charge, the higher the voltage. Lithium iron phosphate batteries (dashed line), by contrast, yield (at best) a truncated version of this pattern -- vast changes in state of charge are accompanied by small changes in voltage. Simply put, voltage measurements cannot be used for all variants of Li-ion batteries.

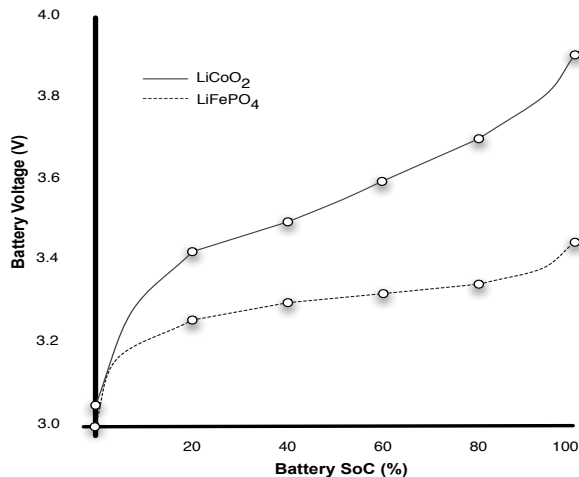


Figure 5 - EMF curves for two different lithium ion chemistries

All told, despite the ease of implementing voltage measurements and EMF estimations to monitor and manage battery systems; in practice, this method is limited in its ability to measure the energy housed in a battery under most conditions.

Coulomb Counting

Another technique that has been implemented in battery management and monitoring is coulomb counting -- quite literally, counting the amount of charge that flows in and out of the battery. Similar to voltage measurements, coulomb counting has intuitive appeal and it is easy to implement (especially with today's μ -controllers). The measurement is made using the following equation:

$$SoC = \alpha - \frac{1}{C_N} \int_0^t \delta I dt \quad ..1$$

Here, α is the initial state of charge, which is typically 100%, C_N is the capacity of the battery, δ is an efficiency rating to account for any loss (typically 1) and I is the flow of current. What is most important is C_N . The value is dynamic and it decreases as the battery's state of health decreases. If the battery is not fully discharged after being maximally charged, then a proper calculation is not possible and the coulomb counter becomes less and less accurate (Coleman et al., 2007). This is a serious shortcoming because, in most instances, it is very rare to fully charge and fully discharge a battery; henceforth, a significant drift in the coulomb counter is difficult to avoid. As the signal drifts, the efficacy of coulomb counting decreases.

Other issues with coulomb counting have been identified, albeit much less problematic. Namely, coulomb counting is less effective when the battery self-discharges or is subject to temperature changes (Aurbach et al., 2002). Moreover, as the battery ages, so too does the efficacy of coulomb counting measurements. Importantly, though, these losses in precision owing to temperature fluctuations and battery aging are of minor consequence when compared to the significant loss in precision that can accompany a drift in the signal: a drifting signal can produce a 100% discrepancy between the measured and actual amount of energy in the battery, whereas these other issues may affect the precision of coulomb counting by less than 1% per month (Takeno et al., 2005).

Resistance

For both voltage measurements and coulomb counting (albeit less so), the state of health of the battery influences the efficacy of battery monitoring and management: new batteries (100% state of health) are easy to gauge, whereas older batteries (85% state of health and below) are notoriously difficult to gauge. To account for changes in state of health, fuel gauging techniques often measure the resistance of a battery as the primary means to index state of health.

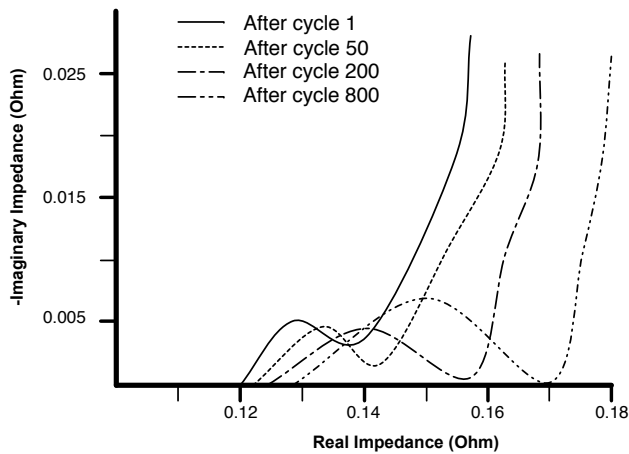


Figure 6 - Complex impedance changes for a lithium cobalt oxide battery

For some Li-ion chemistries, the impedance measured in the battery is an effective way to assess the battery's state of health. As shown in Figure 6, lithium cobalt oxide evidences clear stepwise changes in the real impedance of the battery, as the number of cycles increases.

For other chemistries, impedance measurements are less effective in determining state of health. As highlighted in Figure 7, the impedance measured from lithium manganese oxide batteries yields an ambiguous relationship to the number of cycles the battery has experienced.

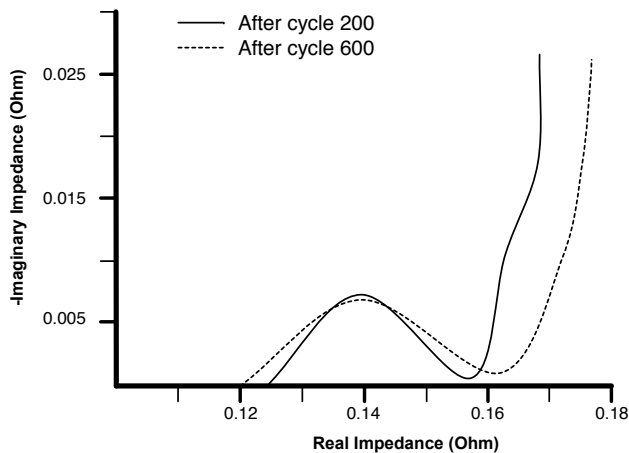


Figure 7 - Complex impedance changes for a lithium manganese oxide battery

Simply put, before resistance measurements can be used to index state of health, one must be assured that a reliable relationship exists between resistance and battery aging; otherwise, there is little purpose in taking impedance measurements.

Another significant issue in using impedance measurements is that a direct coupling exists between state of health and state of charge; namely, as the state of charge of the battery changes, so too does its state of health. This interdependence is highlighted in Figure 8.

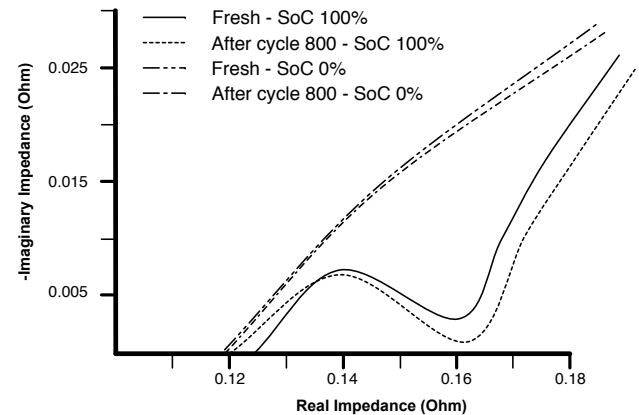


Figure 8 - Complex impedance data as a function of state of charge and state of health

As noteworthy in this figure, the battery's state of charge dominates the impedance spectrum, and makes it difficult to identify the different states of health that are present. The complex methods that one can adopt to tease out state of health from these data are computationally intensive and, as such, impractical for most consumer products or industrial applications. Accordingly, rather than relying on the normal discharge currents, most applications now use an excitation pulse present on the device to assess changes in the impedance spectrum. Although this technique is much more effective for some Li-ion chemistries that show a systematic increase in resistance as the battery ages, it cannot improve the reliability of battery monitoring for chemistries that do not have this relationship.

Direct Magnetic Measurements

Despite differences in chemistry, all Li-ion batteries work in the same basic way -- energy is released when lithium ions diffuse towards the cathode (see Fig. 1). Thus, as the battery discharges, the anode will contain fewer lithium ions (McDowall, 2008). This change in composition can be exploited to directly assess how much energy the battery contains.

The magnetic susceptibility of a substance is an index of the magnetization \mathbf{M} of this substance as it is placed within a particular magnetic field strength \mathbf{H} . This relationship may be restated as,

$$M = xH \quad ..2$$

As highlighted in Table 2, the magnetic susceptibilities of lithium and carbon are very different: lithium is a paramagnetic substance -- its presence will enhance the magnetic field; whereas, carbon is a diamagnetic substance -- its presence will minimize the magnetic field. Importantly, lithium and carbon are the predominant chemistries that are present at the anode of the battery and can be effectively used to index the amount of energy that the battery contains.

Anode Electrode Magnetic Susceptibilities ($\chi_m/10^6 \text{ cm}^3 / \text{mol}$)	
Lithium	14.2
Carbon	-6

Table 2 Negative electrode susceptibilities

To measure this change in magnetic susceptibility, an excitation field is needed to stimulate the metals and a sensor is needed that is capable of registering these minute changes in the magnetic field. To create an excitation field, a coil is used to generate eddy currents. These eddy currents produce magnetic fields that are enhanced by paramagnetic materials or reduced by diamagnetic materials. In the case of Li-ion batteries, an enhancement in the magnetic field indicates that there are more lithium ions at the anode or, in layman's terms, the battery is more fully charged. By contrast, a reduction in the magnetic field indicates that carbon is the predominant chemistry at the anode or the battery is in a lesser state of charge.

By using the definition,

$$\delta = \sqrt{\frac{1}{\pi\mu\sigma f}} \quad ..3$$

we can determine the magnetic field absorption. The degree of penetration into the metal, or skin depth, is given by δ . The permeability of the material is represented by μ and the conductivity by σ . The frequency, f , reflects the depth of the material being sampled. Since equation 1 is inversely proportional, we know that deeper penetration of the material occurs at lower frequencies.

The magnetic field produced by a coil follows Biot-Savart's Law,

$$d\mathbf{B} = \frac{\mu_0}{4\pi} \frac{I d\mathbf{l} \times \hat{r}}{r^2} \quad ..4$$

in which...

$d\mathbf{B}$ represents the vector quantity that describes the magnetic field at the desired point;

I is the current;

$d\mathbf{l}$ is a vector quantity of an infinitesimal current element in the direction of the field potential;

μ_0 is the magnetic susceptibility dependent on the material;

\hat{r} is the unit vector in the direction to where the magnetic field is to be calculated; and

r is the distance to the calculation point.

If we consider a current loop with a radius of R , and we wish to measure the field at a particular point x , the equation can be simplified to:

$$B(x) = \frac{\mu_0 n I R^2}{2(R^2 + x^2)^{3/2}} \quad ..5$$

which allows us to easily assess the material properties of the anode.

A sensor is then used to measure these changes in the magnetic field. Magnetic field sensor technology has changed significantly over the last decade, driven mainly by hard drive read head development. Magnetic tunneling junction sensors are, currently, the state of the art. The sensors are built by separating two metals, CoFeB, by an insulator of MgO that is only a few atoms thick. A biasing voltage is created between the metals, by allowing current to flow across the insulator. The likelihood of quantum tunneling is directly related to electron spin alignment, which can be manipulated and controlled by introducing external magnetic fields, with the following consequence: as the strength of the magnetic field increases, the electron spin alignment increases, and more electrons may tunnel across the insulator. As more electrons tunnel across the insulator, the resistance of the device falls (Schrag et al., 2006). Accordingly, the magnetoresistance of the sensor is the first indication of its performance: for example, anisotropic sensors have 2-3% magnetoresistance, whereas giant sensors have 15-20% magnetoresistance. By contrast, sensors that implement magnetic tunnel junctions have a magnetoresistance of 200% (Schrag et al., 2006).

Finally, a fuzzy logic algorithm is applied to the outputs from the sensor to provide an estimate of the state of charge of the battery.

Efficacy of Direct Magnetic Measurements.

At Cadex Electronics Inc., we have developed a working prototype of this technology, which is patent pending. The algorithm first degausses the coil by running a AC signal at a particular frequency and then reducing the amplitude to zero. A frequency of 20 Hz is then applied and the resultant change in the magnetic field is measured. This degauss-excitation cycle is repeated for number of different frequencies in order to sample a volume of material.

Figure 9 provides a striking example of how changes in the magnetic field correspond to the state of charge of the battery. In this example, a lithium iron phosphate battery was tested during a full charge-discharge cycle, with the magnetic field measurements being probed at 20 Hz.

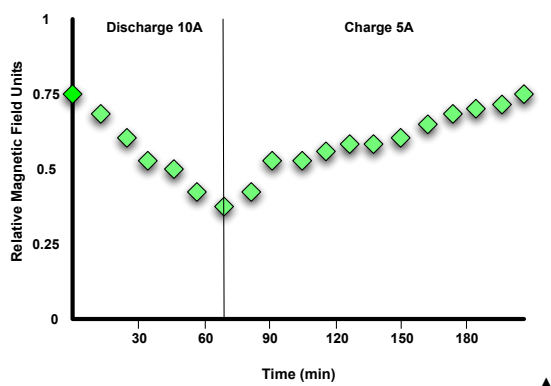


Figure 9 - Magnetic field measurements of a lithium iron phosphate battery undergoing a charge discharge cycle.

Initially the battery was fully charged. Then the battery was discharged at 10A for 300 seconds. Next, the current was removed until the battery was fully discharged. This process was repeated until the battery was fully discharged. Once discharged, the battery was charged using 5A before the battery was charged using constant voltage. As evidenced in this figure, there is a very predominant signal and an excellent correlation evidenced across the entire state of charge.

It is with good reason that I chose a lithium iron phosphate battery to highlight the efficacy of our magnetic sensor. As illustrated in Figure 5 and described above, these batteries are notoriously difficult to monitor -- other techniques that attempt to gauge the amount of energy remaining in these batteries are ineffective. Indeed, the inability to precisely monitor lithium iron phosphate batteries have limited their station in the marketplace. By contrast, our magnetic field

measurements effectively track their state of charge. In fact, the precision is so effective that no data smoothing or computational modeling is necessary to see the pattern -- the raw data show the compelling relationship between state of charge and changes in the magnetic field.

Another Li-ion chemistry that has proven to be difficult to monitor is lithium nickel manganese cobalt oxide -- a type of battery that is often used in electrical bicycles and in medical instruments. Like lithium iron phosphate batteries, the magnetic sensor is very effective in tracking the state of charge of the battery. This effectiveness can be observed in the raw data (not shown, but similar to Fig. 9) and in the calculation of the state of charge (using a fuzzy logic inference algorithm) and the actual state of charge, as shown in Figure 10.

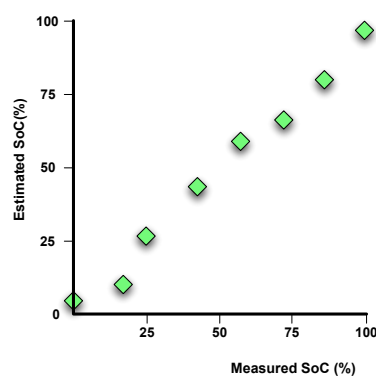


Figure 10 - State of charge estimation using magnetic susceptibility measurements on a lithium nickel manganese battery

As evidenced in this figure, the error with respect to the actual state of charge measurements was significantly less than 5%.

One critical feature of this magnetic sensor technology must be reiterated -- none of these measurements involved voltage data or coulomb counting -- the magnetic sensor directly and precisely measures the ratio of lithium ions and carbon ions at the anode.

Conclusion

Our patented magnetic sensor technology affords several benefits when compared to other battery monitoring techniques: it is more accurate; its accuracy is independent of the age or condition of the battery; and, it allows all Li-ion chemistries to be precisely monitored and managed -- even chemistries that have proven to be difficult to monitor using other techniques. Moreover, the magnetic sensor does not share the same shortcomings as voltage or coulomb counting techniques, insofar that the magnetic sensor does not depend on voltage signals or the current

flow in the battery and it does not require predefined aging models to remain accurate, as do the other techniques. These features of our magnetic sensor technology are factual because we directly measure the battery chemistry as it changes, and relate this information to the user.

One important feature of our new technology has not been mentioned yet, but is noteworthy -- our patented magnetic sensor technology is equally easy to implement and costs approximately the same amount of money to produce as voltage sensors and coulomb counting techniques.

As the world becomes more portable, we are becoming more and more reliant on battery technologies. This trend will only increase because up-and-coming 'green' automotive technologies also emphasize the use of batteries. As we increase our demands of batteries, the necessity to precisely monitor and manage the battery becomes increasingly important. For a moment, imagine the annoyance we have all experienced when a 'fully charged' cellphone or a computer loses its power within minutes. Now imagine the annoyance you might feel if the same situation occurred as you used your car! Such imprecision would and could not be tolerated. At Cadex Electronics, we are developing technologies that assure very precise battery management and monitoring because we do not guess at what is happening inside the battery -- we measure it directly.

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