Chapter 7
Reference Electrodes for Ionic Liquids and Molten Salts

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Acronyms

AAILs	Amino acid ionic liquid
An	Anion
BCr	*Bis*(phenyl)chromium(I) tetraphenylborate
BdMIm	1-Butyl-2,3-dimethylimidazolium
BMIm	1-Butyl-3-methylimidazolium
BOB	*Bis*(oxalatoborate)
BuPy	*N*-butylpyridinium
BzSEt	2-Ethylthiobenzolium
C_4mpyr	*N*-butyl-*N*-methylpyrrolidinium
C_8MIm	1-Octyl-3-methylimidazolium
C_{10}MIm	1-Decyl-3-methyl-imidazolium
Cat	Cation
Cc	Cobaltocene
ChCl	Choline chloride
DEA	Diethanolamine
DIECARB	*N*,*N*-diethylammonium *N'*,*N'*-dialkylcarbamate
dIL	Distillable ionic liquid
DIMCARB	*N*,*N*-dimethylammonium *N'*,*N'*-dialkylcarbamate
DmFc	Decamethylferrocene
DPA	Di-*N*-propylamine

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EAN	Ethyl ammonium nitrate
EMIm	1-Ethyl-3-methylimidazolium
FAP	Tris(pentafluoroethyl)trifluorophosphate
Fc	Ferrocene
FcC_1C_1Im	1-Ferrocenylmethylimidazolium
FcC_1MIm	1-Ferrocenylmethyl-3-methylimidazolium
FcC_1NMe_3	N,N,N,N-trimethylferrocenyl-methylammonium
FcMeOH	Ferrocenemethanol
HMIm	1-Hexyl-3-methylimidazolium
IL	Ionic liquid
ImCl	Imidazolium chloride
Me_4P	Tetramethylphosphonium
$MeBu_3N$	N-methyl,N-tributylammonium
MeCN	Acetonitrile
MEETCARB	N-methyl,N-ethylammonium N',N'-dialkylcarbamate
MEPRCARB	N-methyl,N-propylammonium N',N'-dialkylcarbamate
MIMSBu	1-Methyl-2-butylthiolonium
MIMSEt	1-Methyl-2-ethylthiolonium
mtzSEt	1-Methyl-2-ethylthiotetrazolium
$N_{6,2,2,2}$	Triethyl-hexylammonium
NPr_4	Tetrapropylammonium
OTf	Trifluoromethanesulfonate
$P_{6,6,6,14}$	Trihexyl(tetradecyl)phosphonium
PIL	Protic ionic liquid
PMIm	1-Propyl-3-methylimidazolium
PVdFHFP	Poly(vinylidene fluoride-co-hexafluoropropylene)
QAm	Quaternary ammonium
RTIL	Room temperature ionic liquid
SCE	Saturated calomel electrode
SEI	Solid electrolyte interphase
SHE	Standard hydrogen electrode
TDMATPFPB	Tridodecylmethylammonium tetrakis(pentafluorophenyl)borate
TEA	Triethanolamine
TFSI	*Bis*(trifluoromethylsulfonyl)imide
TMPD	N,N,N',N'-tetramethyl-p-phenylenediamine

7.1   Introduction to Ionic Liquids and Molten Salts

High temperature molten salts and low temperature ionic liquids (RTILs or ILs) share commonalities in that they are both composed of ions in the molten state without any additional solvent. These liquids can act as media for chemical and electrochemical reactions. Indeed since there is a high ionic concentration, these liquids can have beneficial properties for electrochemical studies. Generally wide electrochemical windows and differences in coordination properties mean that

these solvents are useful in particular for deposition of metals that cannot be deposited in molecular solvents, or accessing redox couples not readily investigated in molecular or aqueous solvents. However, there are significant differences between the two which are mainly due to the nature of the ions and the melting temperature and liquidus ranges. For high temperature molten salts these are typically composed of simple salts based on alkali metal-halide or small polyatomic anions whereas low temperature ionic liquids are generally composed of organic cations and inorganic or organic anions where a large degree of covalent bonding exists as well as a charged centre (which may be delocalised over several atoms). Molten salts have been extensively studied as solvents for electrochemical reactions for a large number of years (many decades). Ionic liquids on the other hand are relatively new to the electrochemistry field and have only been studied for the past two decades with any significant efforts.

Since the operating temperature of conventional ionic liquids is close to that of room temperature or for a large proportion of reported liquids below 100 °C, cells and equipment used for electrochemical measurements are similar to those employed with traditional aqueous or non-aqueous solvents. The electrochemical responses of a variety of redox processes have been investigated in ionic liquids and show the importance of these solvent systems in future electrochemical devices and applications.

Molten salt electrochemistry on the other hand has been widely investigated and can be considered a mature field of research. Due to the very high temperatures of operation and general corrosive nature of the molten salts, cells and equipment for electrochemical measurements have by necessity been more complex when compared with those used with traditional aqueous or non-aqueous systems.

To perform electrochemical measurements in both molten salts and ionic liquids, a reliable reference electrode is required when accurate determination of electrode potentials is necessary. For the purposes of this chapter, we will only deal with measurements that are based on a three electrode set-up and not on a two electrode systems. We will first begin by defining both ionic liquids and molten salts before describing the properties of an ideal reference electrode for these systems. After this we shall describe a selected number of literature reports on use of reference electrodes and then finish with a discussion on how to construct reference electrodes for IL and molten salt measurements. Since much of the theoretical treatments are similar to those describing aqueous or non-aqueous reference electrodes we will not go into details, rather refer the reader to the previous sections in this book.

7.1.1 Description of Binary, Ternary or Higher Ionic Liquids/Molten Salts

Ionic liquids are defined as an ionic salt which is liquid in the pure state and is composed solely of cations and anions. Accepted practice within the field is to define ionic liquids as those liquids which have a melting point below 100 °C; however, this is not a ubiquitous definition [1]. Defining ionic liquids in this manner means that many

subclasses of ionic liquids such as protic and distillable are not recognized as ionic liquids. Indeed there is still debate in the field as to a universal definition which can encompass all the subclasses of ILs. At present only the room temperature ionic liquid is strictly defined within the field as an ionic liquid which is liquid at room temperature or below. However, simple changing of cationic or anionic functionalities can significantly affect physical properties such as melting points and electrochemical windows. Furthermore, the number of potential cations and anions which can combine to create an ionic liquid is vast [2]. Thus, it is not difficult to see that the definition of an ionic liquid can encompass a large variety of salts and liquidus temperature regimes. In addition, the boundary in definition between a classical high temperature molten salt such as liquid $NaAlCl_4$ (157 °C) and high temperature ionic liquids is not clearly stipulated within the field. Furthermore, the definition of ILs becomes further complicated when properties such as acidity (Brönsted or Lewis acidity) [3, 4], biological activity (e.g. Amino Acid ILs, AAILs [5]) or stability (e.g. energetic ILs [6]) are taken into account. As such it is important to define an ionic liquid prior to discussing the use of reference electrodes in IL media. Since there is not an accepted field definition of an ionic liquid, we here propose a definition of ILs based on liquidus temperature and physical properties in an attempt to define both ILs and their subclasses of ILs as well as conventional molten salts.

We will first begin by defining the simplest form of an ionic liquid where the IL consists of a binary salt, $[Cat^+][An^-]$, which by and large is the most common class of ionic liquid researched at present. At present the only strictly defined binary IL is the room temperature IL where the salt has to be a liquid at 25 °C. Using this definition we will now define ILs and molten salts based on their liquidus temperatures. Ionic liquids that are liquid at or below 25 °C are defined as RTILs. $NaAlCl_4$ has been extensively studied in the past [7] and is here defined as a molten salt with a melting point of 157 °C [8]. Again by using this point as a fixed reference, we now define a high temperature ionic liquid which has a melting point between 25 and 157 °C. Using this definition we can now encompass the majority of binary ILs that have a higher than room temperature melting point as well as encompassing a proposed higher limit of 100 °C. Above the melting point of $NaAlCl_4$, the conventional/classical molten salts are defined. The definitions are shown diagrammatically in Fig. 7.1. This temperature-based definition also has implications in the complexity of the cations and anions. As the liquidus temperature range is increased the cation and anion molecular complexity is reduced. As the temperature range is increased typically, the level of covalent bonding within the ions decreases and ionic character is increased.

Ternary or higher ionic liquids, where the IL exists as a mixture of cations and/or anions are defined as:

$$[Cat_1^+]_a[An_1^-]_b[Cat_2^+]_c[An_2^-]_d \cdots \tag{7.1}$$
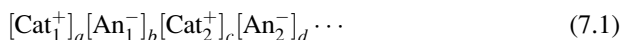
where $a, b, c, d, \ldots = 0, 1, 2, 3, 4, \ldots$ and the subscripts $1, 2, \ldots =$ different ion chemical identity.

Clearly, the binary IL is a subset of this class of IL systems. Hence the melting temperature-based classification system is also applicable for this type of IL. Again
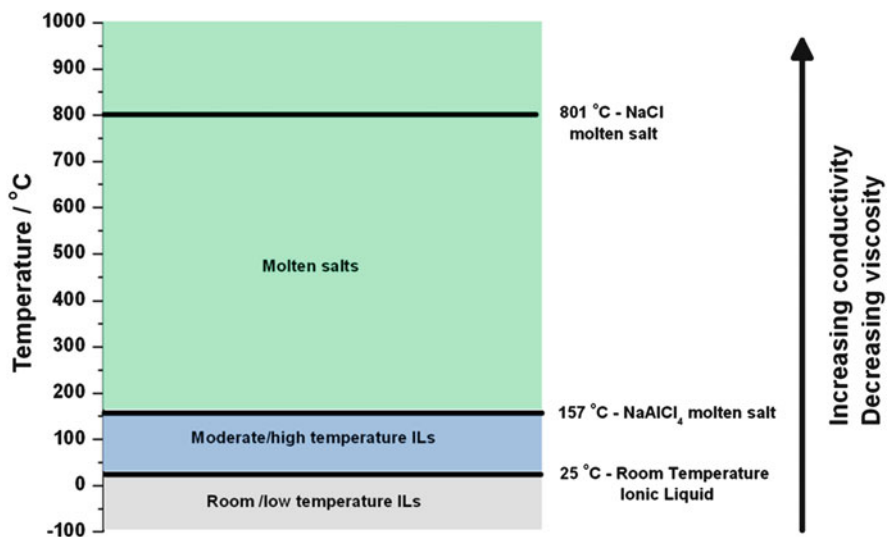
Fig. 7.1 Classification of ionic liquids/molten salts as a function of melting temperature

the two fixed reference points of 25 and 157 °C are used. At this point it is worthwhile noting that for many electrochemical studies on ionic complexes, dissolution of the solute into a binary IL will create a ternary or higher IL system to some extent. The level of higher IL formation will be dependent on the concentration of the solute within the IL media.

Next we define molten salts simply as those salts whose melting temperature is above the 157 °C melting point of NaAlCl₄. Thus we do not differentiate whether the molten salt has a relatively simple ionic structure such as NaCl or NaAlCl₄ or if the ions have a more complex structure typically associated with room temperature ionic liquids. Thus a clear distinction between moderate or high temperature ionic liquids and molten salts can be made. Similar to the distinction between binary and ternary or higher ionic liquids a similar reasoning can be applied to molten salts where mixing of multiple anions and cations can form a ternary or higher molten salt. This then allows the eutectic mixtures of various salts to be classified as molten salts if the melting temperature is above the 157 °C.

7.1.2 Description of Other Subsets of Ionic Liquids

Having defined the distinction between the relatively simple ionic liquid and molten salts we now need to define the subsets of the IL classes. There are literature reports on studies of IL systems where the atypical physical properties such as low/negligible volatility or inertness have been modified. These ILs thus form a subset of the typically studied IL systems. We begin first with the properties of inertness. There

is a class of IL systems which possess either Brönsted or Lewis acidity due to the IL ions interactions. Protic ILs (PILs) are formed by proton transfer between a Brönsted acid and a Brönsted base [1]. PILs are not required to have negligible vapour pressures associated with conventional ionic liquids. The first reported PIL was the ethanolammonium nitrate which had a melting point of 52–55 °C [9]. Since then a large variety of PILs have been reported [3] and a similar spread in melting point and liquidus range exists as compared to conventional ILs.

Lewis acidic ILs have predominantly been restricted within the field to the investigations of ILs where the anion is based on $[AlCl_4]^-$ and its associated complexes. However, a handful of reports have focussed on other anionic structures that can act as a Lewis base or acid [10, 11]. It is evident that if the associated cation with the $[AlCl_4]^-$ anion is Na^+, then the resulting liquid will be the molten salt. Most researchers have focussed on changing the Na^+ to a more functionalised cation, e.g. $[EMIm]^+$, in order to reduce the melting temperature [12]. Thus for both PILs and Lewis acidic ILs, we can also define these systems using the same temperature reference points as shown in Fig. 7.1.

The next major subset of ILs we will discuss is the distillable ionic liquids or dILs. These IL systems have a significant vapour pressure associated with them and at relatively low temperatures can be dissociated into a gaseous or liquid state and can be reformed at lower temperatures [13, 14], hence the distillable nature of them. Clearly this subset of ILs has unique properties that are a cross between conventional molecular solvent systems and also posses the ionic character associated with ILs. Previous work has shown that again, as for the IL and PIL systems, dILs can have a range of melting points. Thus, as before the temperature distinction shown in Fig. 7.1 can be applied to this special case.

It should be noted the PIL and dIL systems have similarities within their physical properties. Namely, both these classes have ionic characters similar to the more conventional IL/molten salts. However, they also posses properties that are more closely related to those of traditional non-aqueous molecular solvents. Based on this we now need to expand the definitions presented in Fig. 7.1 to encompass these properties, and this is presented in Fig. 7.2.

We will limit our definitions of ionic liquids and molten salts to the above major categories. Although other categories or subsets of ionic liquids exist for the purposes of this chapter, it is not necessary to define them in detail as the arguments and recommendations will equally apply to these subsets with minimal modifications.

7.2 Properties of an Ideal Reference Electrode for Use in IL Media

The properties and theoretical aspects of a reference electrode for use in electrochemical measurements have been described elsewhere in detail (Chap. 1). Here we will limit discussion to those specific properties relevant to application in ionic liquid/molten salt systems.
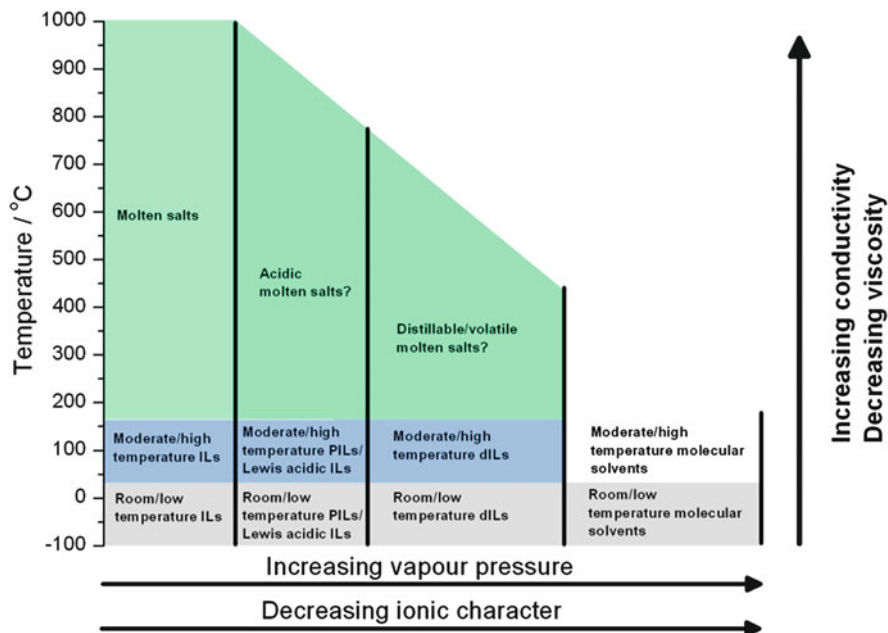
Fig. 7.2 Classification of ionic liquids/molten salts and their subsets as a function of melting temperature

As detailed in Sect. 7.1 there are many classes of ILs each with unique chemical/physical properties and temperature regimes under which electrochemical measurements can be performed. As such, the "holy grail" of a universal reference electrode system for ionic liquids and molten salts cannot exist. For each IL system and operating temperature, careful choice of reference electrode must be made which can operate reliably under the appropriate measurement conditions. Some of the properties to consider are explained in more detail below.

The properties of an ideal reference electrode for IL and molten salt media have been succinctly stated by Barrosse-Antle et al. [15]. First, the reference potential should be stable with time [15], i.e. the reference potential does not drift or shows minimal drift (ideally less than 10 mV per day). A second requirement, as also for non-aqueous and aqueous reference electrodes, is that the reference electrode should have a very small temperature coefficient over the desired operating range [15, 16]. However, for ILs and molten salts this can be a difficult requirement to meet since the liquidus operating range is much larger than for aqueous or non-aqueous systems. Hence, a more accurate statement would be that the reference electrode is stable over the temperature range of data collection. Finally, the reference electrode should be reproducible in its preparation as well as voltage response over the duration of use/measurement as well as being convenient to use [15].

7.2.1 Electrodes of the First Kind

As explained in previous chapters (see Chaps. 1 and 2), an electrode of the first kind is one based on atoms or molecules and their corresponding cation or anion in solution. This type of electrode is most commonly used within the ionic liquids' fields. Requirements for this class of reference electrode are that the atom or molecule used does not react with the ionic liquids. Additionally the corresponding cation or anion should be stable in the solvated form within the IL and should not have any corresponding undesirable chemical reactions with the IL components. If the reference electrode is based on a metal M|metal ion M^{n+} electrode system, and assuming the activity of the metal is 1 (which may not be true for specific cases), then the corresponding potential of the half-cell is given by:

$$E = E_c^{\ominus\prime} + \frac{RT}{nF} \ln a(M^{n+}), \tag{7.2}$$

where E is the measured potential, $E_c^{\ominus\prime}$ the formal potential, R the gas constant, T the temperature, n the number of electrons transferred and a is the activity of the species.

If the reference electrode is based on a gas, G_x, and its corresponding cation or anion in solution $\frac{1}{x}G^n$, then the corresponding potential of the half-cell is given by

$$E = E_c^{\ominus\prime} + \frac{RT}{nF} \ln \frac{a(G^n)}{f_{G_x}^{1/x}}, \tag{7.3}$$

where f is the fugacity of the gas ($f = \gamma p$ where p is the pressure and γ is the fugacity coefficient) and all other symbols are defined in Eq. (7.2).

Clearly similar requirements exist for gas-based reference electrodes. The corresponding gas ions must not react with the IL components to form alternative products.

For both metal-based or gas-based reference electrodes, these definitions in practical terms mean that the concentration of the dissolved ions within the reference electrode remains essentially constant. The electrochemical changes of the reference system should be part of an equilibrium reaction and overall no net reaction should occur during the measurement. However, if a reaction or alternative equilibrium occurs which can change the activities of the reference species in a detectable manner, then the redox couple chosen can be problematic and stability of the reference electrode can be compromised. Therefore, care must be taken to ensure this type of reaction does not take place with the chosen ions.

7.2.2 Electrodes of the Second Kind

Reference electrodes of the second kind are based on three phases in mutual contact where the electrode potential is a function of the common anion (An^-) activity in solution. One such example is the Ag|AgCl|Cl$^-$ (silver–silver chloride) reference electrode and as stated in previous chapters this type of electrode is well known in aqueous electrochemistry. The electrode potential of the half-cell is given by:

$$E = E_c^{\ominus\prime} - \frac{RT}{nF} \ln a(An^-).$$

(7.4)

Use of this type of reference electrode requires good solubility and high concentrations of the anion, An^-, in the IL. This is not always straightforward for ILs, where limited or low solubility of anions such as halides (e.g. Cl$^-$) may be encountered. As a result this type of reference electrode is not commonly used within IL electrochemistry. Another requirement is that the metal halide solid, typically on the surface of the metal wire, should be stable to the IL and should have very low solubility within the IL, otherwise unstable reference electrode potentials will arise. This can be mitigated by having a suitably high concentration of the An^- in the IL phase.

There are a number of reports where the Ag|AgCl reference electrode (where the AgCl phase is deposited onto a Ag wire) is used without addition of Cl$^-$ to the IL phase. This type of electrode is not an electrode of the second kind and is actually a quasi-reference electrode (see Chap. 14). As such this type of reference electrode may show significant drift since lack of Cl$^-$ in the IL phase means that over time the Cl$^-$ and Ag$^+$ on the electrode will diffuse into the IL phase causing a shift in reference potential.

7.2.3 Inert Electrode Immersed in a Solution Containing a Soluble Redox Couple

This class of reference electrode consists of an inert conducting or semi-conducting material immersed in an IL solution containing a redox couple:

$$Ox + ne^- \rightleftharpoons Red.$$

(7.5)

Provided that the redox equilibrium (7.5) is electrochemically reversible under potentiometric conditions at the inert electrode, the electrode will assume a potential given by the following equation (Nernst equation):

$$E = E_c^{\ominus\prime} + \frac{RT}{nF} \ln\left(\frac{a(Ox)}{a(Red)}\right).$$

(7.6)

Use of this type of electrode with ILs requires that both sides of the redox couple chosen are soluble in the IL system. Furthermore as with the previous classes of electrodes, the IL must not react chemically or electrochemically with the redox couple to produce unwarranted products. Lastly, the redox reaction chosen must exhibit electrochemical reversibility within the IL. Due to the nature of many IL interactions with analytes, this should be confirmed prior to using this type of electrode. Since the reference electrode may be required to operate over a wide temperature regime, the redox couple should also exhibit electrochemical reversibility over the temperature range required.

7.2.4 Experimental Considerations for an Ideal Reference Electrode in IL Electrochemistry

For the majority of IL systems reported, the physical properties of the IL mean that issues such as solution resistance become significant. This is much more apparent for IL measurements than compared to non-aqueous solvents or aqueous solvent systems. Barosse-Antle et al. have summarised the physical properties relevant to electrochemistry of a range of ILs [15], and this is summarised in Table 7.1. As is evident from Table 7.1, IL conductivities (which are related to solution resistance as explained below) are lower than those of organic solvents resulting in high resistances.

The effect of solution resistance, IR_u, on the IUPAC recommended cobaltocene| cobaltocenium (Cc|Cc$^+$) [17] and decamethylferrocene|decamethylferrocenium (DmFc|DmFc$^+$) couples in two different IL media is shown in Table 7.2. For both redox couples the peak–peak separation should be 57 mV at the reported temperatures. As can be seen from the data, this is not always the case even when appropriate levels of IR_u compensation have been applied by the potentiostatic software.

In order to minimise effects of IR_u, care should be taken to locate the reference electrode as close as possible to the working electrode. In Fig. 7.3a, this is shown schematically. Ideally the distance between the working and reference electrodes, x, should be minimised without contacting the two electrodes. There are two types of commonly used reference electrode assemblies used in the IL field. The first is where a porous glass or Vycor$^®$ frit is used within a glass chamber and separated from the electroactive species by a fritted tube or compartment (Fig. 7.3b), while the second is where the compartment/tube is replaced with a Luggin capillary (Fig. 7.3c).

In IL electrochemistry use of the two commonly reported types of reference electrodes shows significant difference in electrochemical responses. Using the methodology developed by Oldham [19], the level of R_u can be calculated as a function of distance of the reference electrode tip from a disk working electrode by:

$$R_u = \frac{\arctan[x_{R-W}/r_w]}{2\pi r_w \kappa}, \tag{7.7}$$

Table 7.1 Physical properties relevant to electrochemistry of a range of ionic liquids (data from [15] and references therein)

Ionic liquid	η (cP)	ρ (g cm^{-3})	κ (mS cm^{-1})	Electrochemical window (V)
Binary ionic liquids				
[EMIm][TFSI]	34	1.53	8.8	4.3
[BMIm][TFSI]	52	1.44	3.9	4.8
[BdMIm][TFSI]	105	1.42	2.0	5.2
[HMIm][FAP]	74	1.56	1.3	5.3
[C$_4$mpyr][TFSI]	89	1.4	2.2	5.2
[BMIm][OTf]	90	1.3	3.7	4.9
[BMIm][BF$_4$]	112	1.21	1.7	4.7
[N$_{6,2,2,2}$][TFSI]	167	1.27	0.67	5.4
[BMIm][PF$_6$]	371	1.37	1.5	4.7
Brönsted acidic ionic liquids				
[DEA]Acetate	336	1.22	0.14	2.4
[DPA][OTf]	19	0.97	1.19	2.7
[TEA]Acetate	11	0.96	1.27	3.4
[DEA]Cl	305	1.24	0.86	4.0
Distillable ionic liquids				
DIMCARB	77	1.05	1.7	2.0
DIECARB	14	0.91	0.053	2.1
MEETCARB	85	0.98	0.37	1.9
MEPRCARB	70	0.95	0.18	1.8
Organic solvents				
Acetonitrile	0.34	0.79	7.6[a]	5.0[a]
N,N-Dimethylformamide	0.92	0.94	4.07[a]	4.3[a]
Dimethylsulphoxide	1.99	1.10	2.7[a]	4.4[a]

Where η = viscosity, ρ = density and κ = conductivity
[a]Data for 0.1 M [NBu$_4$]ClO$_4$/solvent solutions at 295 K

Table 7.2 Comparison of peak separations for IUPAC recommended reference compounds (and their derivatives) at macro working electrodes in IL media from cyclic voltammetry measurements

Scan rate (mV s^{-1})	ΔE_{peak} (V) for 1.8 mM DmFc|DmFc$^+$ in DIMCARB [13]	ΔE_{peak} (V) for 5 mM Cc|Cc$^+$ in [C$_4$mpyr][TFSI] [18]
2	65	–
5	–	63
10	58	64
20	57	65
40	60	–
50	–	74
100	64	80

where x_{R-W} is the reference electrode–working electrode distance, r_w the electrode radius and κ is the solution conductivity.

Figure 7.4a shows the calculated R_u level using Eq. (7.7) for various sizes of disk working electrodes in an IL with conductivity of 2.2 mS cm^{-1} (for example butyl-methylpyrrolidinium[TFSI] [20]). It is clear from Fig. 7.4a that the level of R_u is
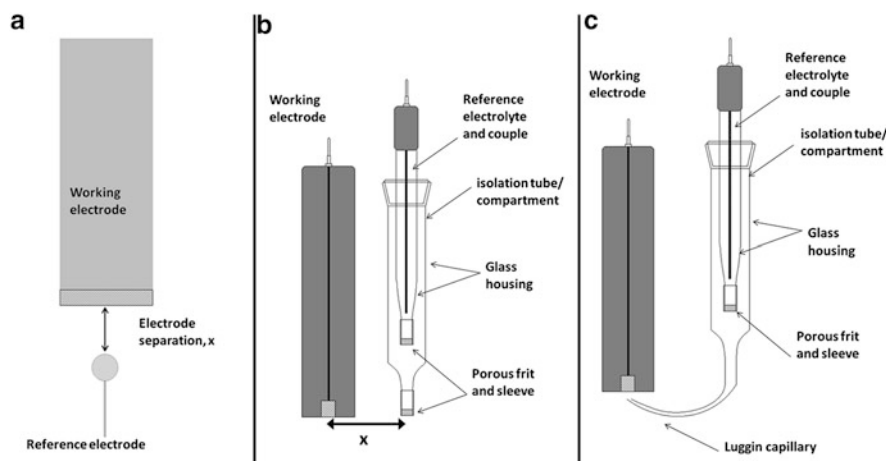
Fig. 7.3 Location of reference electrodes within an electrochemical cell and types of electrode assemblies commonly reported in the literature. (**a**) Schematic showing separation of reference and working electrode; (**b**) porous glass or Vycor® fritted reference electrode separated from the electroactive species by a fritted tube or compartment and (**c**) porous glass or Vycor® fritted reference electrode separated from the electroactive species by a tube/compartment fitted with a Luggin capillary
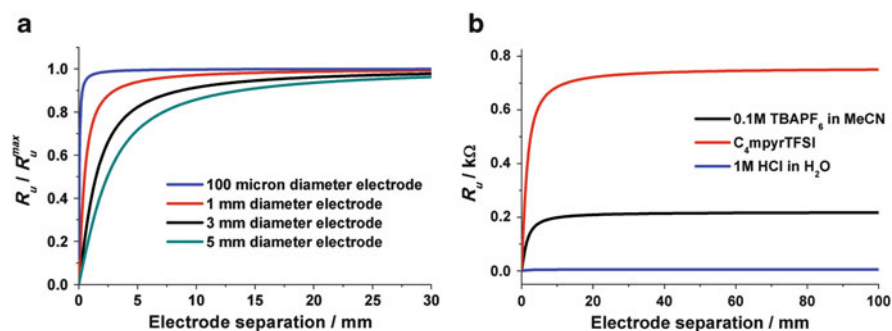

Fig. 7.4 (**a**) Effect of electrode separation on R_u in butyl-methylpyrrolidinium[TFSI] (data normalised to allow comparisons); (**b**) Effect of solution conductivity on R_u for 1 M HCl in water ($\kappa = 33$ S m^{-1} [21]), 0.1 M [NBu$_4$]ClO$_4$ in acetonitrile ($\kappa = 7.6 \times 10^{-3}$ S m^{-1} [15, 21]) and butyl-methylpyrrolidinium TFSI ($\kappa = 2.2 \times 10^{-3}$ S m^{-1} [15, 20])

dependent on both the working electrode size and distance between the reference electrode and working electrode. However, above 20 mm separations a steady state in the R_u values is achieved for an IL with conductivity of 2 mS cm^{-1}. Experimentally this means that the reference electrode placement in IL electrochemical measurements more than 20 mm from the working electrode results in the level of R_u being essentially constant. In other words, the working and reference electrodes are essentially at infinite distance from each other. The second thing to

notice from Fig. 7.4a is for macrosized (1–5 mm diameters) disk working electrodes the region where R_u can be minimised is in the 5–10 mm separation region or below. Again practically this means that a choice of correct reference electrode assembly must be made prior to measurements. For many frit type of reference electrodes (e.g. glass tubes with a Vycor® frit), the frit size itself results in a minimum separation of several millimetres. This in combination with placement of the reference electrode within the cell can result in several millimetre separations. As a result the R_u value can be close to the infinite linear region. Experimentally in order to get electrode separations <5 mm, it is wise to use a Luggin type of reference electrode assembly (see Fig. 7.3). Regardless, whichever electrode assembly type the readers wish to use, care should be made when reporting or analysing electrochemical data in IL media to ensure that any IR_u effects are accounted for or minimised.

It can be seen from Fig. 7.4b that there is a significant effect on R_u when using an ionic liquid electrolyte as compared to aqueous or non-aqueous electrolytes. This is due to the difference in conductivities of ionic liquids when compared to aqueous or non-aqueous electrolytes. Consequently, electrochemical data measured in ionic liquid media will have an inherently higher level of IR_u issues. Thus, reference electrode construction and placement in order to minimise IR_u effects is critical when using IL electrolytes.

7.3 Reference Electrode Systems Used with IL and Molten Salt Media

Although reference electrodes are important for measurements of accurate potentials in electrochemical measurements, little attention has been spent on development of ionic liquid reference electrodes. The following sections will discuss the types of reference electrodes reported within the ionic liquid field or discuss redox systems, which can be modified for use in reference electrodes.

7.3.1 Room Temperature Ionic Liquid Reference Electrodes

7.3.1.1 Ag|Ag⁺ Reference Electrode

By far the most commonly reported reference electrode system for room temperature or low temperature binary, ternary or higher reference electrodes has been based on the Ag|Ag⁺ couple. Some selected examples of reference electrodes using the Ag|Ag⁺ couple in selected ILs are presented in Table 7.3. All of these reported reference electrodes are based on use of a silver wire immersed into an IL containing a dissolved silver salt.

Table 7.3 Selected Ag|Ag$^+$ reference electrodes used in binary, ternary or higher IL media

Ionic liquid	Silver salt	Electrode assembly	Calibrated potential (mV)	Reference
[EMIm][TFSI]	0.1 M AgOTf	Frit	+440 (vs. Fc|Fc$^+$)	[22]
[BMIm][BF$_4$]	AgNO$_3$/MeCN/RTIL	Frit	−232 (vs. Fc|Fc$^+$)	[23]
[BMIm][TFSI]	AgNO$_3$/MeCN/RTIL	Frit	−182 (vs. Fc|Fc$^+$)	[23]
[BMIm][PF$_6$]	AgNO$_3$/MeCN/RTIL	Frit	−222 (vs. Fc|Fc$^+$)	[23]
[C$_4$mpyr][TFSI]	10 mmol L^{-1} AgOTf/ [C$_4$mpyr][TFSI]	Frit	+390 (vs. Fc|Fc$^+$)	[24]
[EMIm][OTf]	10 mmol L^{-1} AgOTf/ [C$_4$mpyr][TFSI]	Frit	+416 (vs. Fc|Fc$^+$)	[24]
[EMIm][EtSO$_4$]	10 mmol L^{-1} AgOTf/ [C$_4$mpyr][TFSI]	Frit	+432 (vs. Fc|Fc$^+$)	[24]
[BMIm][BF$_4$]	10 mmol L^{-1} AgOTf/ [C$_4$mpyr][TFSI]	Frit	+418 (vs. Fc|Fc$^+$)	[24]
[BdMIm][BF$_4$]	10 mmol L^{-1} AgOTf/ [C$_4$mpyr][TFSI]	Frit	+415 (vs. Fc|Fc$^+$)	[24]
[C$_4$mpyr][BOB]	10 mmol L^{-1} AgOTf/ [C$_4$mpyr][TFSI]	Frit	+401 (vs. Fc|Fc$^+$)	[24]
[C$_4$mpyr][TFSI]	10 or 100 mMol L^{-1} AgOTF	Frit	+475 (vs. Ag|AgNO$_3$)	[25]
[C$_4$mpyr][TFSI]	10 or 100 mMol L^{-1} AgTFSI	Frit	+470 (vs. Ag|AgNO$_3$)	[25]
[C$_4$mpyr][TFSI]	10 or 100 mMol L^{-1} AgNO$_3$	Frit	+460 (vs. Ag|AgNO$_3$)	[25]
[BMIm][TFSI]	10 mMol L^{-1} AgOTf	Frit	+387 (vs. Fc|Fc$^+$)	[26]
[MeBu$_3$N][TFSI]	10 mMol L^{-1} AgOTf	Frit	+340 (vs. Fc|Fc$^+$)	[26]
EAN	Ag/AgNO$_3$	Frit	+114 (vs. Fc|Fc$^+$)	[27]
[C$_4$mpyr][TFSI]	Ag/AgCl/KCl (aqueous)	Frit	−320 (vs. Fc|Fc$^+$)	[28]
[BMIm][TFSI]	Ag/AgCl/KCl (aqueous)	Frit	−320 (vs. Fc|Fc$^+$)	[28]
[TDMA] [TPFPB]	Ag/AgCl	Luggin	Not reported	[29]
ChCl	Ag/AgCl/urea/ChCl	None	Not reported	[30]
ChCl	Ag/AgNO$_3$/urea/ ChCl	None	Not reported	[30]

It is clear from Table 7.3 that the reference potential of the Ag|Ag$^+$ couple is dependent on the choice of ionic liquid and also choice of silver salt used for construction of the reference electrode. This is observed in the potential values of the IUPAC recommended Fc|Fc$^+$ couple [17], which are in the range of −440 to 320 mV against the Ag|Ag$^+$ couple. As such it is recommended that once a reference electrode has been constructed, the reference potential is calibrated against an IUPAC recommended internal reference couple. In order to minimise the variations in the reference electrode potential, it is important to dissolve the Ag$^+$ solution into the same IL as used for the electrochemical measurements, otherwise, a junction potential (ΔE_j) will exist which needs to be determined. For example Snook et al. have constructed an Ag|AgOTf|[C$_4$mpyr][TFSI] reference electrode

Table 7.4 Plots of ΔE_j for the Ag|AgOTf|[C$_4$mpyr][TFSI] reference electrode in a variety of ILs [26], where $E_c^{\ominus\prime}$ is the formal potential and ΔE_j is the liquid junction potential

Ionic liquid	$E_c^{\ominus\prime}$ (mV) for Fc|Fc$^+$ vs. Ag|AgOTf|[C$_4$mpyr][TFSI] electrode	ΔE_j (mV)
[C$_4$mpyr][TFSI]	-390	0
[EMIm][OTf]	-146	-26
[BMIm][BF$_4$]	-418	-28
[EMIm][EtSO$_4$]	-432	-42
[BdMIm][BF$_4$]	-415	-25
[C$_4$mpyr][BOB]	-401	-11

and have measured its ΔE_j in a variety of ILs by determination of the Fc|Fc$^+$ potential [27]. As can be observed from Table 7.4, significant shifts in the ΔE_j exist. In order to minimise this situation when using an Ag|Ag$^+$ reference system, the silver salt should be dissolved into the same IL as used for the electroactive species, and similarly the same IL should be used within the salt bridge tube or compartment.

As stated in Sect. 7.2.1 of this chapter, for electrodes of the first kind, the metal ions should not react with the ILs. Basile et al. have noted that the presence of water results in the formation of silver nanoparticles for solutions of Ag$^+$ ions dissolved into [C$_4$mpyr][TFSI] [31]. These authors postulate that this occurs via chelation of Ag$^+$ by the [TFSI] anion and a subsequent disproportionation reaction in the presence of water to form a Ag^{2+}-[TFSI] complex and Ag^0 [31]. Thus, the choice of a reference electrode based on Ag|AgOTf|[C$_4$mpyr][TFSI] may be problematic. The authors did note that over a short period of time, when chemical reaction rates were low, the Fc|Fc$^+$ reversible potential was close to that reported by Snook et al. [27, 31]. According to Snook et al. [27] the Ag|AgOTf|[C$_4$mpyr][TFSI] reference electrode is only stable for 3 weeks before the solution needs to be replaced and the electrode remade. Therefore, if the Ag|Ag$^+$ couple is to be used in other ILs, then any potential chemical reactions of Ag$^+$ ions within this IL should be explored prior to use, as well as the stability of the reference electrode over time.

Experimentally, the Ag|Ag$^+$ reference electrode is constructed by dissolution of the silver salt into an IL. This IL solution is then placed into either a fritted tube or into a Luggin capillary tube. The electrical contact is then made via a silver wire immersed into the Ag$^+$/IL solution. In the case of the fritted tube, this should ideally be separated from the electrochemical cell by use of a second fritted tube or compartment depending on cell design, containing only neat IL which is the same for the electroactive species. This is done in order to minimise effects of any potential leakage of silver ions from the reference electrode.

Although adoption has not been widespread, Kakiuchi et al. have constructed a Ag|AgCl|[C$_8$MIm][TFSI] gel reference electrode [32]. This system is created by anodising an Ag wire in KCl to form a surface layer of AgCl. Onto this layer a solution of [C$_8$MIm][TFSI] containing PVdF HFP (400,000 Da) as a gelling agent in acetone is coated. The IL is then gelled on the surface by evaporation of the acetone solvent. This gelled RTIL-coated electrode is then used as a reference

Table 7.5 Formal potential of the H$^+$|HAn couple and peak potential (E_p) for the HAn $\rightarrow$ ½ H$_2$ + An$^-$ reduction in ionic liquid media

Ionic liquid	E_p (V) for the HAn $\rightarrow$ ½ H$_2$ + An$^-$ reduction	$E_{c,2H^+/H_2}^{\ominus\prime}$ for the H$^+$|HAn couple
[EMIm][TFSI]	1.18 (HTFSI)	1.36
[BMIm][TFSI]	1.19 (HTFSI)	1.36
[BMIm][OTf]	0.68 (HOTf)	0.98
[N$_{6,2,2,2}$][TFSI]	1.08 (HTFSI)	1.30
[BMIm][PF$_6$]	1.24 (HPF$_6$)	1.53
[P$_{6,6,6,14}$][TFSI]	0.73 (HTFSI)	1.38

All potentials referenced to Cc$^+$|Cc^0 [32]

electrode by placing into a salt bridge tube/compartment containing the same IL as that used for the electroactive species. The $E_c^{\ominus\prime}$ of this reference electrode is estimated by Kakiuchi et al. to be 0.22 V vs. SHE [32].

7.3.1.2 H$_2$|H$^+$ Reference Electrode

Although strictly speaking this type of reference electrode has not been used in IL electrochemistry, sufficient data does exist for this type of reference electrode to be constructed. Compton et al. have shown that H$_2$ can be oxidised in a number of ILs at a platinum electrode (Table 7.5) [33–35]. Additionally for selected ILs the reduction of H$^+$ can also occur [35]. The formal potential determined for the H$^+$|H$_2$ redox couple in selected ILs is presented in Table 7.5.

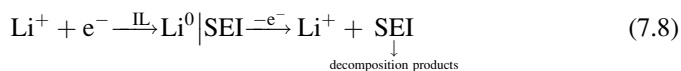As can be seen from Table 7.5, similar to the case of the Ag|Ag$^+$ couple, when the H$_2$|H$^+$ is referenced to an internal redox couple a shift in the $E_c^{\ominus\prime}$ occurs and is dependent on the IL studied. Additionally, Compton et al. have reported that the electrochemical reversibility of the H$_2$|H$^+$ couple is dependent on the identity of the IL [33]. This is most likely due to the difference in proton activity in the different ILs. As such it is important if the reader wishes to use the H$_2$|H$^+$ couple in a reference electrode; then the reversibility of this reaction is checked prior to use.

Experimentally constructing an H$_2$|H$^+$ reference electrode in IL media would be similar to construction of the Ag|Ag$^+$. In this particular case a platinum wire should be used and the Ag$^+$ solution replaced with an H$^+$ solution. The separation of the reference electrode via a salt bridge tube of compartment (depending on cell designs) is advisable in order to minimise issues with leakage of reference solution into the electroactive solution. Experimentally the set-up would be similar to that used in PILs electrochemistry (see below for further details)

7.3.1.3 Li|Li$^+$ Reference Electrodes

A number of researchers have reported on the use of lithium wires or lithium foils as reference electrodes (see [36] and references therein). Experimentally researchers

usually directly immerse the lithium foil into the IL solution of interest. Whilst this reference electrode can provide a stable reference point for electrochemical measurements, it is not possible to consider this type of electrode as anything other than a quasi-reference electrode. A well-known phenomenon on the lithium electroplating reaction is the formation of a passivating film known as the solid electrolyte interphase (SEI) layer. Thus, the lithium redox couple should be defined as:

$$Li^+ + e^- \xrightarrow{\;IL\;} Li^0 \big| SEI \xrightarrow{\;-e^-\;} Li^+ + \underset{\underset{\text{decomposition products}}{\downarrow}}{SEI} \qquad (7.8)$$

Since the SEI formation can occur both chemically and frequently electrochemically in ionic liquid media, there will be a shift in the potential of the Li|Li$^+$ couple. However, the chemical composition of the SEI layer is frequently unknown and thus the shift in potentials cannot be readily ascertained without calibration. Further complications exist when using lithium electrodes as reference electrodes. Compton et al. have studied the Li|Li$^+$ couple at both Ni and Pt electrodes. For the Li|0.1 M LiAsF$_6$|[C$_4$mpyr][TFSI] reduction of Li$^+$ occurs at -3.2 V vs. Fc|Fc$^+$ at a Ni electrode [37]. Using a combination of simulation and experimental methods, Compton et al. have determined the formal potential of this reaction to be -3.25 V vs. Fc|Fc$^+$ and is stable between 25 and 45 °C [37]. In [Me$_4$P][TFSI] the lithium redox couple has been observed at -3.20 V vs. Fc|Fc$^+$ at a glassy carbon electrode [38], and this potential correlates well with that reported by Compton et al. but does show a difference of 50 mV most likely due to the existence of a different composition of SEI layer. Another potential drawback of using a Li|Li$^+$ reference electrode is highlighted in the work of Yang et al. where use of lithium foils as both working and counter electrodes results in chemical reaction between the lithium metal and the IL [39]. Consequently, Yang et al. report that voltametric features were detected due to the generation of electroactive impurities from the chemical reaction [39].

7.3.1.4 Quasi-reference Electrodes

Quasi-reference electrodes (Chap. 14) are by and large the most common type of reference electrodes reported in ionic liquid electrochemistry. However, since the potential of this reference electrode is unknown, and the stability of this reference electrode can vary from electrode to electrode and solution to solution, accurate potentials cannot be measured with this type of reference electrode. Quasi-reference electrodes can also show considerable drift, especially when using silver wire directly immersed into the IL solution [15]. If using a quasi-reference electrode in IL electrochemical measurements for accurate determination of potentials, the electrode should be calibrated against an IUPAC recommended redox couple [15]. However, in many IL electrochemical reports, this is not performed and as such any potential data reported cannot be confirmed by other laboratories.

A large variety of quasi-reference electrodes have been used based on metal wires such as silver [40], platinum [41], aluminium [42], tungsten [43], magnesium [44], etc. Typically electrodes are placed directly into the IL solution or separated from the main solution inside a fritted glass tube/compartment. In order to minimise liquid junction potentials in the latter case, the same ionic liquids as per the measurements is used as electrolyte. It is the authors' experience that separation of the quasi-reference electrode allows for a reduction in potential drift when compared to direct insertion into the electrochemical cell.

7.3.2   Redox Reference Electrodes

Many researchers have reported on the use of either Ag|Ag$^+$ reference electrodes or quasi-reference electrodes in IL media. In order to standardise reference potentials, some researchers have used the IUPAC recommended ferrocene or cobaltocene couples or derivatives of these. Indeed, there is some debate in the literature which advocates that IL electrochemical measurements be reported against these redox couples. Tables 7.6, 7.7 and 7.8 show the potentials of ferrocene, its derivatives and cobaltocene in IL media.

For all of the measurements reported in Table 7.6, experimentally they were accomplished by dissolution of ferrocene in the concentration range of 1–50 mM into the IL of choice and after dissolution measurements performed. For the majority of the data presented in Table 7.6 this was collected via analysis of cyclic voltammetric experiments. Consequently, the voltammetric peak potentials were used in order to determine the $E_c^{\ominus\prime}$ values or the $E_{1/2}$ values. Experimentally $E_{1/2}$ values can be converted to $E_c^{\ominus\prime}$ values as shown below (under conditions where $\alpha = 0.5$ and $D_{\text{ox}} = D_{\text{red}}$):

$$E_{1/2} = E_c^{\ominus\prime} - \frac{RT}{F} \ln \left(\frac{D_{\text{ox}}}{D_{\text{red}}} \right)^{1/2}. \tag{7.9}$$

This methodology can be used to calibrate potentials if the assumption is adopted that the Fc|Fc$^+$ couple is unaffected by solution. However, there are a number of issues that can prevent the calibration process. First, in some IL systems ferrocene has been reported to not have ideal electrochemistry or indeed chemically react with IL components [13, 46]. In a scenario such as this, use of the Fc|Fc$^+$ couple is not recommended for calibration purposes. Second, the effect of solvation on Fc may not be negligible and may cause a shift in potentials [45]. Therefore, the assumption that the Fc|Fc$^+$ couple is unaffected by solution may not be accurate. Consequently, prior to use of Fc its electrochemistry should be explored in detail to determine if it can be used within the IL system under investigation. A much more serious issue has been explored by Compton and co-workers. This group

Table 7.6 Potentials of ferrocene in selected IL media

Ionic liquid	Compound and concentration	$E_c^{\ominus\prime}$ (mV)	Reference
[BMIm][TFSI]	Fc (various concentrations)	77 vs. Ag|Ag$^+$ (320 vs. SCE)	[45]
[BMIm][PF$_6$]	Fc (solid adhered to electrode surface)	+1,332 vs. Cc|Cc$^+$	[46]
[EMIm][TFSI], [MIMSBu][TFSI], [MIMSEt][TFSI], [MIMSBu] [PO$_2$(OBu)$_2$], [BzSEt][PO$_2$(OET)$_2$], [mtzSEt][PO$_2$(OEt)]$_2$, [MIMSEt][OTf], [MIMSBu][OTF], [MIMSEt][PF$_6$]	3 mM Fc	770 vs. Ag wire QRE	[47]
0.95:1 AlCl$_3$:[ImCl]	20 mM Fc	+654 vs. Ag wire QRE	[48]
0.8:1 AlCl$_3$:[ImCl]	15 mM Fc	+806 vs. Ag wire QRE	[48]
0.6:1 AlCl$_3$:[ImCl]	40 mM Fc	+863 vs. Ag wire QRE	[48]
0.45:1 AlCl$_3$:[ImCl]	50 mM Fc	+863 vs. Ag wire QRE	[48]
[EMIm][BF$_4$]	4.39 mM Fc	+477–481 vs. Ag|Ag$^+$| cryptand RE (dependent on electrode material)	[49]
[BMIm][BF$_4$]	5 mM Fc	+324 vs. SCE	[50]
[BMIm][PF$_6$]	5 mM Fc	+176 vs. SCE	[50]
[BMIm][BF$_4$]	1 mM Fc	+375 vs. Ag|AgCl	[51]
[EMIm][TFSI]	1 mM Fc	+230 vs. SCE (reported as $E_{1/2}$)	[52]
[PMIm][TFSI]	1 mM Fc	+258 vs. SCE (reported as $E_{1/2}$)	[52]
[BMIm][TFSI]	1 mM Fc	+270 vs. SCE (reported as $E_{1/2}$)	[52]
[HMIm][TFSI]	1 mM Fc	+250 vs. SCE (reported as $E_{1/2}$)	[52]
[BdMIm][TFSI]	1 mM Fc	+309 vs. SCE (reported as $E_{1/2}$)	[52]
[BuPy][TFSI]	1 mM Fc	+280 vs. SCE (reported as $E_{1/2}$)	[52]
[BuPy][BF$_4$]	1 mM Fc	+370 vs. SCE (reported as $E_{1/2}$)	[52]
[BMIm][BF$_4$]	1 mM Fc	+370 vs. SCE (reported as $E_{1/2}$)	[52]
[BMIm][PF$_6$]	1 mM Fc	+270 vs. SCE (reported as $E_{1/2}$)	[52]
[C$_4$mpyr][TFSI]	5 mM Fc	−390 vs. Ag|AgOTf| C$_4$mpyrTFSI	[24]
[EMIm][OTf]	5 mM Fc	−416 vs. Ag|AgOTf| C$_4$mpyrTFSI	[24]
[BMIm][BF$_4$]	5 mM Fc	−418 vs. Ag|AgOTf| C$_4$mpyrTFSI	[24]
[EMIm][EtSO$_4$]	5 mM Fc	−432 vs. Ag|AgOTf| C$_4$mpyrTFSI	[24]
[C$_4$mpyr][BOB]	5 mM Fc	−401 vs. Ag|AgOTf| C$_4$mpyrTFSI	[24]

Table 7.7 Potentials of ferrocene derivatives in selected IL media

Ionic liquid	Compound and concentration	$E_c^\ominus$ (mV)	Reference
[EMIm][TFSI]	3 mM [FcC$_1$MIm][TFSI]	−263 V vs. Ag|Ag$^+$	[55]
[BMIm][PF$_6$]	Fe(CpCH$_3$)$_2$ (solid adhered to electrode)	+1,233 vs. Cc|Cc$^+$	[46]
[BMIm][PF$_6$]	Fe(CpCOCH$_3$)$_2$ (solid adhered to electrode)	+1,813 vs. Cc|Cc$^+$	[46]
[BMIm][PF$_6$]	CpFeCpCOH (solid adhered to electrode)	+1,627 vs. Cc|Cc$^+$	[46]
[BMIm][PF$_6$]	Fe(Cp(CH$_3$)$_5$)$_2$ (solid adhered to electrode)	+856 vs. Cc|Cc$^+$	[46]
[BMIm][PF$_6$]	10 mM CpFeCpCH$_2$CH$_3$	+1,285 vs. Cc|Cc$^+$	[46]
[EMIm][TFSI], [MIMSBu] [TFSI], [MIMSEt][TFSI], [MIMSBu][PO$_2$(OBu)$_2$], [BzSEt] [PO$_2$(OET)$_2$], [mtzSEt] [PO$_2$(OEt)$_2$], [MIMSEt][OTf], [MIMSBu][OTf], [MIMSBu]Cl	5 mM Fe(Cp(CH$_3$)$_5$)$_2$	−510 vs. Fc|Fc$^+$	[47]
[C$_n$C$_1$Im][TFSI] (n = 2, 4 or 8)	FcMeOH	250 vs. Ag QRE	[56]
[EMIm][TFSI]	[FcC$_1$Im][TFSI]	105 vs. Fc|Fc$^+$	[57]
[EMIm][TFSI]	[FcC$_1$NMe$_3$][TFSI]	234 vs. Fc|Fc$^+$	[57]
[EMIm][TFSI]	[FcC$_1$C$_1$Im][TFSI]	168 vs. Fc|Fc$^+$	[57]
[EMIm][TFSI]	1 mM DmFc	−310 vs. SCE (reported as $E_{1/2}$)	[52]
[PMIm][TFSI]	1 mM DmFc	−260 vs. SCE (reported as $E_{1/2}$)	[52]
[BMIm][TFSI]	1 mM DmFc	−250 vs. SCE (reported as $E_{1/2}$)	[52]
[HMIm][TFSI]	1 mM DmFc	−250 vs. SCE (reported as $E_{1/2}$)	[52]
[BdMIm][TFSI]	1 mM DmFc	−214 vs. SCE (reported as $E_{1/2}$)	[52]
[BuPy][TFSI]	1 mM DmFc	−250 vs. SCE (reported as $E_{1/2}$)	[52]
[BuPy][BF$_4$]	1 mM DmFc	−30 vs. SCE (reported as $E_{1/2}$)	[52]
[BMIm][BF$_4$]	1 mM DmFc	−80 vs. SCE (reported as $E_{1/2}$)	[52]
[BMIm][PF$_6$]	1 mM DmFc	−210 vs. SCE (reported as $E_{1/2}$)	[52]

measurements on ferrocene under a flow of inert gas or increasing temperature show that ferrocene can volatilise from some ILs [53, 54]. Previously Vorotynsev and co-workers have suggested using UV/vis spectroscopy to determine the exact concentration of ferrocene in the IL solution prior to making measurements [45].

Indeed if Eq. (7.9) is to be used to determine the $E_c^{\ominus\prime}$, then it is important to know the exact concentration of ferrocene in order to determine the diffusion coefficients of the oxidised and reduced forms.

These reports would suggest that for some IL systems, ferrocene can be used for calibration of potentials. However, prior to proceeding with this technique it is advisable that the electrochemical response of ferrocene is checked in the IL system under investigation in order to determine if ferrocene can be used. If the ferrocene is not behaving as an ideal reference couple, then use of derivatised ferrocenes or cobaltocene, or alternative redox couples is suggested. There can also be problems with dissolving enough ferrocene in the IL of interest to carry out the cyclic voltammetry. Ferrocene is largely insoluble or only partially soluble in many ILs.

In cases where use of ferrocene is compromised due to poor electrochemical reversibility of chemical reactions with IL functionalities, then some researchers have proposed use of derivatised ferrocenes. A list of either the standard potentials or midpoint potentials for a series of derivatised ferrocenes is given in Table 7.7. In many cases the derivatised ferrocenes show more stable electrochemical response and less reaction with IL components. Consequently, they have been used to calibrate potentials in ILs either as a standard of choice or as a replacement for ferrocene. The methodology in use of these complexes is the same as for ferrocenes. After dissolution of the complexes in the IL, the potential is measured (usually but not limited to voltametric techniques) and from this the $E_c^{\ominus\prime}$ determined and hence calibrate potentials. If the ferrocene or derivatised ferrocene redox processes are in the same potential range as those of the electroactive species, alternative redox couples should be used.

In those instances where use of ferrocenes or derivatised ferrocenes is problematic due to non-ideal electrochemistry of the metallocenes or overlap of potentials with those of electroactive species making potential calibration problematic, the cobaltocene|cobaltocinium couple has been suggested as a reference redox couple [15]. The Cc|Cc$^+$ couple is also an IUPAC recommended redox couple for electrochemical potential calibration [17]. Table 7.8 lists selected data for the Cc|Cc$^+$ couple in IL media. The cobaltocene electrochemical response is similar to that of the ferrocenes and the methodology of calibration is again similar. Many researchers typically use the same voltametric techniques as discussed for the ferrocene and derivatised ferrocene couples to determine the $E_c^{\ominus\prime}$ value for the Cc|Cc$^+$ couple.

An alternate redox reference compound to metallocenes has been proposed by Compton and co-workers [25]. The redox chemistry of N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) is two electron transfer processes as shown below:

$$TMPD \rightleftarrows TMPD^{+\bullet} + e^- \tag{7.10}$$

$$TMPD^{+\bullet} \rightleftarrows TMPD^{2+} + e^- \tag{7.11}$$

Table 7.8 Potentials of cobaltocene in selected IL media

Ionic liquid	Compound and concentration	$E_c^{\ominus\prime}$ (mV)	Reference
[BMIm][PF$_6$]	10 mM CcPF$_6$	−1,146 vs. Ag|Ag + QRE	[46]
[EMIm][TFSI], [MIMSBu] [TFSI], [MIMSEt][TFSI], [MIMSBu][PO$_2$(OBu)$_2$], [MIMSEt][OTf], [MIMSBu] [OTf], [MIMSEt][PF$_6$], [MIMSBu]Cl	Cc	−1,340 vs. Fc|Fc+	[47]
[EMIm][BF$_4$]	5.13 mM CcPF$_6$	−608 to 858 vs. Ag|Ag$^+$|cryptand (reported as $E_{1/2}$ dependent on electrode material)	[49]
[C$_4$mpyr][TFSI]	5–100 mM CcPF$_6$	−1,737 to −1,706 (reported as $E_{1/2}$ dependent on electrode material)	[18]

Table 7.9 Potential of TMPD vs. Ag\|10 mmol Ag$^+$ or calibrated to the Cc\|Cc$^+$ couple

Ionic liquid	$E_{1/2}$ vs. Ag|Ag$^+$ (mV)	$E_{1/2}$ vs. Cc|Cc$^+$ (mV)
[EMIm][TFSI]	167	1,076
[BMIm][TFSI]	498	1,069
[C$_4$mpyr][TFSI]	186	1,088
[N$_{6,2,2,2}$][TFSI]	242	1,079
[BMIm][BF$_4$]	166	1,093
[BMIm][PF$_6$]	183	1,092

All potentials determined from cyclic voltametric measurements

The first redox process has been determined to be reversible in [C$_4$mpyr][TFSI], [P$_{6,6,6,14}$][TFSI], [C$_{10}$MIm][TFSI] and [EMIm][TFSI] and has a faster rate of electron transfer then the Ag\|Ag$^+$ couple in [C$_4$mpyr][TFSI] [25]. In a variety of ILs investigated by Compton et al., the potential of this process [Eq. (7.10)] against Cc\|Cc$^+$ and the Ag\|Ag$^+$ reference is shown in Table 7.9.

As can be seen from Table 7.9, the potential difference between the Cc\|Cc$^+$ couple and the TMPD first redox process is constant for the ILs tested. The approximate 20 mV shifts observed are most likely due to experimental uncertainties. Thus, the TMPD complex offers an alternative to the ferrocene or cobaltocene couples for reference potential calibration. If the potential of the TMPD couple is close to that of the electroactive species, then use of the *bis* (phenyl)chromium(I) tetraphenylborate (BCr) redox couple with ILs has also been proposed by Lewandowski et al. [49]. Studies of this redox reference compound in [EMIm][BF$_4$] show that it has a stable potential at +0.236 to +0.248 V vs. Cc\|Cc$^+$ (range dependent on electrode material) [49].

Experimentally, both the TMPD and BCr complexes potentials are determined from solutions of <10 mM in the IL using voltametric techniques. The electroactive species is then referenced to the determined potentials of the reference couple.

An alternative reference couple based on the $I^-|I_3^-$ couple has been used by Bonhôte and co-workers [58] and also Matsumoto and co-workers [59, 60] to evaluate the electrochemical windows of a range of ionic liquids. This reference electrode was calibrated to the ferrocene couple in [EMIm] trifluoroacetate and found to have a potential of -0.195 V vs. Fc|Fc$^+$ [58]. Experimentally this reference electrode is constructed by dissolution of 15 mM I_2 and 60 mM NPr$_4$I in an ionic liquid and electrical connection via an inert Pt wire. The reference solution and Pt wire are separated from the electroactive species via use of a fritted glass tube.

7.3.3 Moderate or High Temperature Ionic Liquid Reference Electrodes

Thus far we have discussed reference electrodes that have been used primarily at room temperature or close to room temperature. However, there are many IL systems that exhibit liquidus ranges starting above room temperature. This increase in operating temperature poses significant problems for choice of reference electrode. Thus, far the majority of literature reports have used quasi-reference electrodes based on metallic wires. Indeed calibration of these reference potentials is complicated by the increase in temperature. If the temperature is suitably high enough, then use of metallocenes such as ferrocene is not possible due to evaporation of ferrocene from the IL medium. Compton and co-workers have shown that if the temperature is increased, then ferrocene evaporation can take place at a rate dependent on operating temperature (this also occurs under a flow of inert gas, though at a lesser rate) [53, 54]. Indeed this work has shown the rate constants for ferrocene evaporation increase almost fivefold upon increase of temperature from 25 to 37 °C [53, 54].

Similar effects were noted by Bhatt et al. on electrochemical studies of ILs at elevated temperatures [38]. However, the operating temperature of 190 °C meant that only a single voltametric scan of ferrocene could be achieved prior to evaporation, whereas studies at the temperatures investigated by Compton et al., should allow for several more scans albeit with a constantly decreasing ferrocene concentration. Bhatt et al. used the Li$^+$|Li^0 (via dissolution of LiTFSI into the IL) couple in combination with a quasi-reference electrode for calibration purposes. Since at 190 °C, lithium is liquid (hence effects of SEI formation are negligible) and calibration could be achieved. However, as will be shown in the following section, increasing temperature further results in formation of intermetallic complexes, and the electrochemical response of lithium differs at significantly elevated temperatures.

7.3.4 Molten Salt Reference Electrodes

Experimental techniques for handling high temperature molten salts have been developed for many more years than those for room temperature ionic liquids. Considerable experimental challenges need to be overcome to find a stable reference electrode that will survive high temperatures (often up to 1,000 °C) and highly corrosive molten salt environments.

7.3.4.1 Quasi-reference Electrodes for Molten Salts

In the harsh environment of a high temperature molten salt, it is often necessary to resort to quasi-reference electrodes. Examples of this approach include the use of a stable metal or graphite dipped into the molten salt being investigated [61–67]. The use of quasi-reference electrodes rely on a close to constant environment of ions maintaining a similar potential for long periods, i.e. a stable environment of ions in which the potential will not drift significantly with electrolysis time. Of course, long-term stability is rarely achieved and only an approximate indication of potential is usually possible using this strategy. Some of these studies used an internal standard redox couple to determine the initial position of the reference electrode [65–67]. In electrochemical studies, however, there is often a need to use a reference electrode to avoid uncertainty in which electrochemical processes are occurring [68].

7.3.4.2 Ag|Ag$^+$ Reference Electrode for LiCl–KCl Eutectics

For electrochemical studies involving LiCl or LiCl–KCl (eutectic mix) molten salts, generally the reference electrode of choice is a Ag|Ag$^+$ based reference electrode [69, 70]. Typically, this reference electrode is constructed with a silver wire immersed in 1 mol% AgCl in the LiCl–KCl eutectic melt which is contained within the reference electrode casing. However, Shirai et al. [70] suggest that 1–10 mol% is much more stable. Work by this group [70] suggests that the positive shift in potential with prolonged use (typically seen in experiments) is a result of a decrease of the AgCl concentration. The experimental observation of the reference electrode shows a black stain at the closed end of the Pyrex tube as well as dendritic Ag metal growth. The origin of the concentration loss is attributed to the escape of Ag$^+$ and minute Ag particles into the closed-end tube by ion exchange and absorption or attributed to the reaction between Ag$^+$ and the O^{2-} in the melt to form silver oxide (Ag$_2$O) precipitate.

The electrochemical reaction for the Ag|Ag$^+$ reference electrode for molten salt experiments is as follows [70]:

$$Ag^+{}_{(molten\ salt)} + e^-{}_{(Ag\ wire)} \rightleftarrows Ag_{(Ag\ wire)} \qquad (7.12)$$
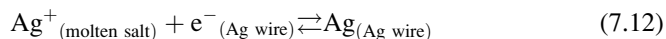
Studies by Shirai et al. [70], look at the temperature dependence of the reversible potential of the reference electrode versus a Cl$^-$|Cl$_2$ reference electrode (see later section for description of this electrode). They find that the potential is slightly lowered compared to what is theoretically expected by complexation of the Ag$^+$ ions with the chloride (Cl$^-$) ions in the melt, which lowers the activity of Ag$^+$ ions.

This reference electrode is used in other eutectic chloride melts. Another example is MgCl$_2$–NaCl–KCl [71]. Here the reference electrode utilised contained 0.01 mol% AgCl in a LiCl–KCl eutectic. In other words, two different melts were used—where the one in the reference compartment is different to the one in the working compartment. This will create junction potentials, and if the reference electrode is not properly characterised, this will be a problem.

7.3.4.3   Sealed Ag|AgCl Reference Electrode for Calcium Chloride Melts

The typical set-up of a reliable Ag|AgCl reference electrode for molten chloride melts is shown in Fig. 7.5 as a schematic representation. This involves a thinned and sealed lower end of the quartz tube which acts as an ion conducting membrane. This thin wall is achieved using glass blowing while the bottom is in the flame. The wall thickness is controlled by the blowing operation. Above this thin-walled membrane is the much thicker quartz tube. While this tube is still open, a silver wire attached to a longer piece of tungsten wire is inserted within the glass and subsequent to this the electrolyte (typically a mixture of AgCl, NaCl, KCl at a molar ratio of 10:45:45) is added so that it rests in the bottom of the arrangement. This long quartz tube is then sealed (under vacuum) around the tungsten wire in the middle of the tube using a hydrogen–oxygen flame. This means the reference compartment is sealed, which overcomes the problem of the molten chloride volatility. More details of the construction are given in reference [68]. Although the reference electrode is referred to as a Ag|AgCl electrode, technically it is a Ag|Ag$^+$ electrode as there is no AgCl coating on the electrode. However, it is arguable whether the traditional classifications of reference electrodes are applicable to molten salts. This particular reference electrode is affected by the coordination of chloride anions around the silver cations. If the molten salt was a fluoride-based molten salt, the reference potential would be different. This would not be the case, for example, in non-aqueous reference electrodes as, in general, the solvent molecules solvate the silver cation and negate the effect of anions on the potential of the reference electrode.

Fig. 7.5 Ag|AgCl reference
electrode schematic
for chloride baths
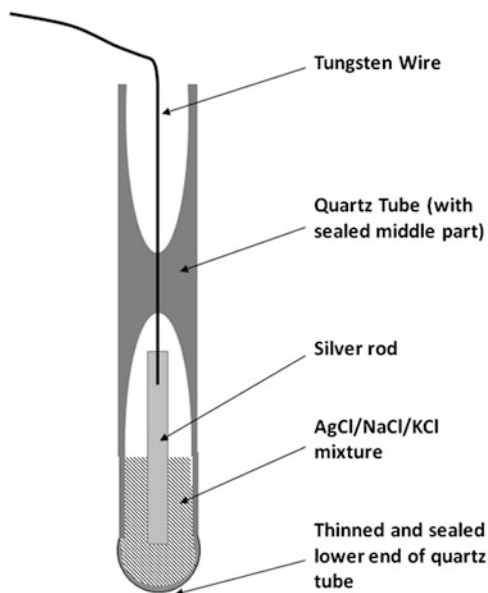
This reference electrode system is suitable for use between 700 and 950 °C, below which the reference system has too high impedance (typically above 10^4 Ω) and above which the silver melts ($T_m = 962$ °C). Internal standards are used to measure the stability of the electrode. Here, reduction of silicon dioxide and calcium metal deposition (from Ca^{2+}) can be used as indicator potentials and show that the electrode can give stable potentials for times between hours and days. In practice, while carrying out long electrolysis reactions in chloride melts, the group at CSIRO (Australia) have found that the electrodes typically last about 8 h. This is, however, sufficient to carry out many types of experiments.

The other stability test carried out by Gao et al. [68] was to add AgCl and KCl to a level of 10 wt% to the molten salt melt. These had insignificant effect on the potential of the reference electrode. However, addition of small amounts of NaCl affected the potential of the reference electrode by 0.1522 V per decade. This is related to the changing concentration of Na^+, as well as Ca^{2+}, which indicates conduction of these ions through the membrane and a build up of a junction potential. Multiple reference electrodes constructed by the group [68] (by different workers) resulted in reference electrodes with potentials varying no more than 15 mV but typically with a variance smaller than 8 mV.

7.3.4.4 Li|Li⁺ Reference Electrodes

Work by Okabe et al. [72, 73] utilises a Li|Li⁺ reference electrode for the study of additions of Li_3N into molten LiCl at 900 K. This reference electrode was constructed by passing a current of 2 A for 100 s between a nickel sheath cathode

and a graphite anode immersed in LiCl. This results in lithium metal plated in-situ onto the nickel electrode as an intermetallic compound. Further deposition (longer deposition times) would result in growth of Li metal as liquid due to the low melting point of lithium (180.5 °C). In all, these experiments, with addition of Li_3N to the bath the lithium deposition process onto either a nickel or molybdenum working electrode [as described in Eq. (7.13) below], resulted in a reversible potential at 0 V vs. the $Li|Li^+$ reference electrode [72]. Therefore, the reference electrode was believed to be stable during the measurements.

$$Li^+ + e^- \rightarrow Li(\text{on Ni, Mo}) \tag{7.13}$$
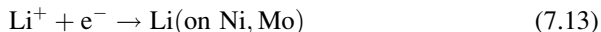
7.3.4.5 $Al^{3+}|Al$ Reference Electrode for Eutectic Chlorides

Another less commonly used reference electrode for eutectic mix chloride melts is the $Al^{3+}|Al$ reference [70], where an aluminium wire is utilised in an $AlCl_3$ (e.g. 0.419 mol%) mixture in the LiCl–KCl salt.

7.3.4.6 $Cl^-|Cl_2$ Reference Electrode for Chloride Melts

A standard reference electrode for chloride melts is shown in schematic form in Fig. 7.6. This is the standard chlorine or $Cl^-|Cl_2$ reference electrode [70, 74, 75]. This electrode is analogous to the standard hydrogen electrode (SHE) for aqueous solutions. Here the gas (Cl_2) is passed over the reference compartment chloride melt at 1 atm (standard pressure), and the potential of the reference system is determined by the ratio of the chloride concentration to the chlorine gas pressure as described in the Nernst equation. As with the SHE this is a difficult reference electrode to maintain and utilise and is consequently less commonly used in modern experiments. In the work by Shirai et al. [70], the reference electrode is used as a standard reference point for measuring other reference electrode potentials. Sometimes the measurements are done using, for example, a $Ag|Ag^+$ reference electrode and then converted to the standard chlorine scale [76, 77]. This is much like aqueous results being shifted to the SHE scale even though the measurements were not done using this reference electrode.

7.3.4.7   Nickel-Based Reference Electrodes

The Ni–Ni(II) couple is used as a reference electrode because it exhibits Nernstian behaviour [78–80]. However, diffusion of the strongly oxidising Ni^{2+} into the test solution is a problem. This couple can be used in fluoride melts.

**Fig. 7.6** $Cl^-|Cl_2$ reference
electrode for chloride
eutectics
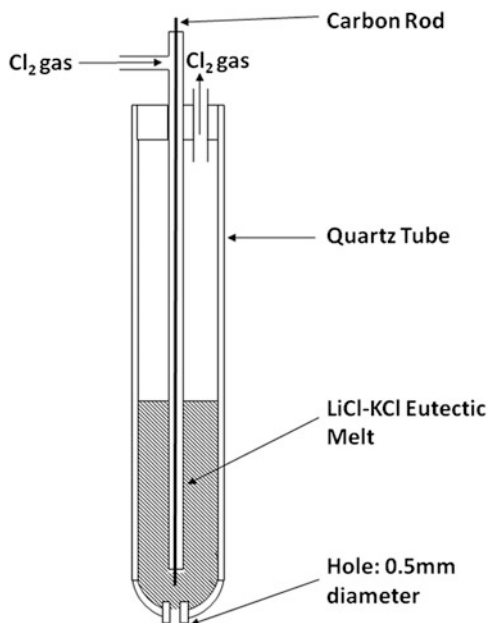
7.3.4.8 $Al_2O_3|Al$ Reference for Cryolite

Perhaps the most difficult molten salt environment for reference electrode survival
and maintenance of key qualities of robustness and stability is sodium cryolite
(Na_3AlF_6), often termed the "Universal Solvent". This molten salt is the only
solvent that can appreciably not only dissolve alumina (to allow electrowinning
of aluminium metal) but also dissolves most other materials used for reference
electrode casings. Thus, the reference electrode of choice for this particular molten
salt almost invariably is a quasi-reference electrode such as carbon (often the
graphite crucible housing the molten salt itself) or a metal (for example molybdenum or tungsten).

However, there have been suggestions in the literature for reference electrodes
based on the alumina|aluminium couple. An electrode comprising a molten salt and
aluminium was first described by Drossbach [81]. Common types of reference
electrodes involve a molten aluminium pool covered by molten cryolite contained
within a thin walled tube of sintered alumina or boron nitride. This housing must be
electrically insulating but able to transfer ions (i.e. porous and ionically conductive). Also it must be resistive to corrosion. Electrolytes must be in contact and a
tortuous path is required such that the different melts do not mix but establish a
stable liquid junction.

This requires a medium from which aluminium can be reversibly deposited and
stripped and consequently requires some form of cryolite in the reference compartment along with aluminium metal. There are two main types of reference electrodes
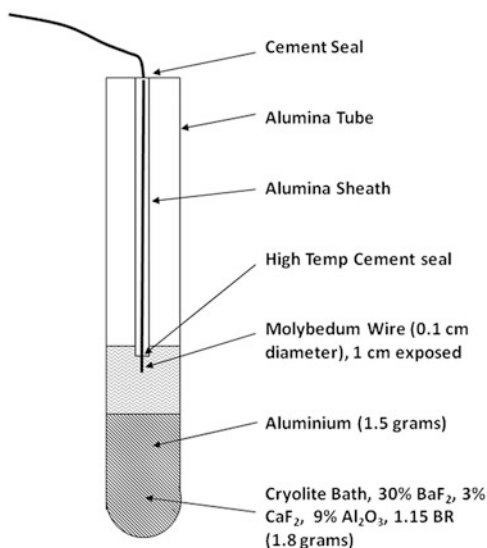suggested for aluminium research in cryolite. The distinction between the two types

Fig. 7.7 Wetted molybdenum hook (WMH) design reference electrode for cryolite [82]
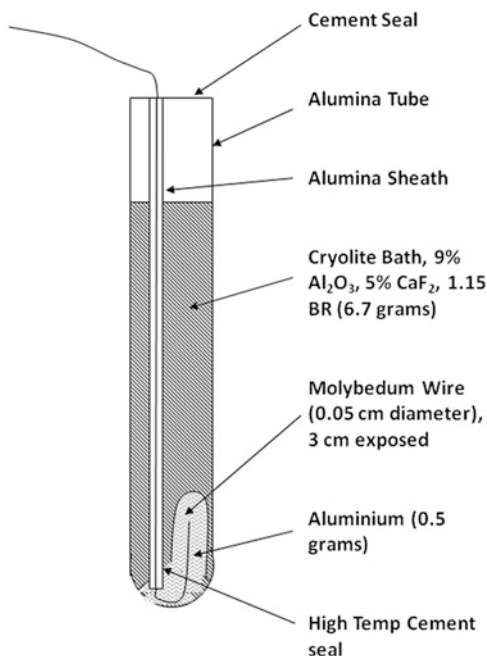
of reference electrode is based on whether the aluminium rests at the bottom of the cryolite bath (this utilises a standard cryolite bath) and is referred to as the wetted molybdenum hook (WMH) design reference electrode by Burgman et al. [82] (Fig. 7.7) or the aluminium floats above the cryolite bath (this utilises a modified bath of high density) known as the densified bath inverted (DBI) design reference electrode [82] (Fig. 7.8).

The standard bath in the reference electrode by Burgman et al. [82] contains 9 wt % alumina, 5 wt% CaF_2 and a bath ratio (NaF:AlF_3 molar ratio) of 1.15 as shown in Fig. 7.7. The reference potential is established (according to the Nernst equation) by the ratio of the concentration of the saturated Al_2O_3 (~8–9 wt%) and the activity of the aluminium liquid (assumed to be constant and at unity). The mechanism of conversion of Al_2O_3 to Al metal is much debated [83] and involves complex fluoride intermediates, but for simplicity sake the potential can still be considered to be derived from the concentration ratio of alumina to aluminium. This experimental set-up, according to the literature [82], is stable for measurements as long as 8 hours and is reliable to within 5 mV. In this particular work [82] the alumina tube was partially protected from dissolution (alumina is soluble in cryolite) by a surrounding boron nitride block. This alumina tube is found to be porous enough and this combined with the Na^+ content in the alumina means that it can establish a liquid junction and operate as a reference electrode. This so-called wetted molybdenum hook (WMH) design was considered the successful of the two types and is recommended by Burgman et al. [82].

Fig. 7.8 Densified bath inverted (DBI) design reference electrode for cryolite, where aluminium floats above the cryolite bath (modified bath of low density) [82]

Cement Seal

Alumina Tube

Alumina Sheath

High Temp Cement seal

Molybedum Wire (0.1 cm diameter), 1 cm exposed

Aluminium (1.5 grams)

Cryolite Bath, 30% BaF_2, 3% CaF_2, 9% Al_2O_3, 1.15 BR (1.8 grams)

The problem with contact between the electrolyte and lead wire is the partial dissolution (e.g. tungsten wire) and the resulting mixed potential that is established. CaF_2 and BaF_2 can be mixed with the bath to increase the density of the bath or Li, Na, K, Ru, Ce, etc. can be mixed with aluminium to lower the density of the metal so that the aluminium liquid floats above the bath material and contact is made between the tungsten wire and the molten Al. The densified bath for the densified bath inverted (DBI) design described in [82] utilises a high BaF_2 content to increase the density above that of the aluminium liquid metal. Again the potential is established by the ratio of alumina to aluminium liquid according to the Nernst equation. This design was found to be stable for measurements as long as 8 hours and was reliable to within 10 mV. This DBI design was not deemed as reliable by the authors [82] as the WMH design. However, the patent by Sadoway et al. [84] which came out at a similar period of time to the work by Burgman et al. [82] claims the best design for an aluminium reference electrode uses a densified bath due to the lack of contact of the cryolite bath with the tungsten wire.

7.3.5 Brönsted Acidic, Lewis Acidic and Distillable IL Reference Electrode Systems

7.3.5.1 Brönsted Acidic Ionic Liquids

Electrochemical measurements using protic or Brönsted acidic ILs as electrolytes have not received as high a research effort as observed for binary or ternary IL systems. Nevertheless, the proton mobility within these systems results in simplification of reference electrodes available for use.

Some researchers have reported on use of a silver wire quasi-reference electrode (Ag|Ag$^+$ couple) [85–87]. Experimentally this is accomplished by direct immersion of the silver wire into the PIL of interest. Bond and co-workers have reported the electrochemical response of cobaltocene and ferrocene in PILs using this reference electrode [85]. They have shown that the Cc|Cc$^+$ couple is −1.34 V vs. Fc|Fc$^+$. However, they do note that the ferrocene can react chemically with the PIL moieties whereas the cobaltocinium cation does not appear to exhibit this reaction on the electrochemical timescale [85].

An alternate reference electrode based on H$_2$ has also been developed by a number of groups [88–90]. This area is split into two broad sections. The first area is the reversible hydrogen electrode where a platinum wire is inserted into the PIL in a glass tube with a Luggin capillary [88, 89]. Into this reference compartment, H$_2$ gas is bubbled. Since there are available protons within the PIL, the reference couple becomes the H$^+$|H$_2$ reference system. The experimental set-up is shown schematically in Fig. 7.9.

An alternative variation of this reference system is the Pd–H reference electrode [90]. For this system a Pd wire is sealed into a soda glass tube and cycled at 100 mA cm^{-2} in H$_2$SO$_4$ (aq) solution to adsorb H$_2$ onto the surface [91]. After this preparative step, the reference electrode is cleaned in distilled water and placed into the PIL system of interest. This electrode demonstrates stable reference potentials for ca. 24 h and has a reference potential value of +35 mV vs. SHE [90, 91].

An alternate reference system to that of the H$_2$ electrode is the Ag|AgCl reference electrode. Due to the difference in solvation ability of PILs compared to ILs, the dissolution of halide salts such as KCl is far more readily accomplished. As such some researchers have constructed Ag|AgCl|KCl (saturated in PILs) reference electrode systems [92, 93]. This reference electrode exhibits a very stable potential of 0.216 V vs. SHE [92, 93]. Experimentally the reference electrode is constructed by placing a silver wire with a AgCl surface layer into a reference compartment containing a saturated solution of KCl in the PIL of choice.

7.3.5.2 Lewis Acidic or Basic Ionic Liquids

Ionic liquids based on chloroaluminates (the most common form of Lewis acidic or basic ionic liquids) are formed by reacting a quaternary ammonium chloride salt [QAm]$^+$ with aluminium chloride (AlCl$_3$) in various ratios [94]. Common examples are 1-ethyl-3-methyl imidazolium chloride ([EMIm]Cl) and 1-(1-butyl)pyridinium chloride ([BuPy]Cl) [95]. A Lewis base, neutral species or acid is formed by varying the ratio of the two components of the ionic liquid. Using the letter N to represent the mole fraction of AlCl$_3$ in the melt [96], the following classification is given for these ionic liquids:

$N < 0.5$: Lewis base, excess chloride from QAmCl present
$N = 0.5$: Neutral, with [QAm]$^+$ and [AlCl$_4$]$^-$ present

Fig. 7.9 Diagram of a
reversible hydrogen electrode
for PIL electrochemistry [88]
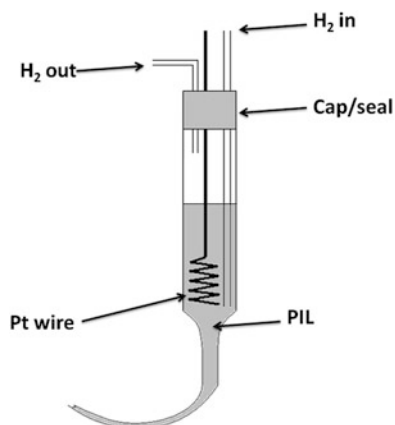
$N > 0.5$: Lewis acid, with $[AlCl_4]^-$ present along with polymeric forms such as $[Al_2Cl_7]^-$ and $[Al_3Cl_{10}]^-$

The most commonly used reference electrodes in these IL types have used a fritted compartment with an aluminium wire dipped into a melt with a fixed N value. Literature examples [96–103] commonly use an aluminium wire in an $N = 0.60$ (acidic melt) ionic liquid, which is also referred to as a 1.5:1.0 QAm$^+$: AlCl$_3$ ratio. A slight variation in the reference half-cell with 66.7 mol% of AlCl$_3$ was used to match the melt of interest in work by Xu et al. [95]. In all cases, a major aluminium species in the melt is $[Al_2Cl_7]^-$ from which aluminium can be deposited and stripped off from the wire. This means the electrode is a reference electrode of the first kind (M|M^{x+}) or (Al|Al^{3+}).

7.3.5.3 Distillable Ionic Liquids

Distillable ILs are formed from combination of CO_2 (or in principle other gases) and dialkyamines to form dialkycarbamates. In a correct stoichiometric ratio of CO_2 to amine, simple dialkycarbamate salts are formed [13]. However, if the CO_2 is limited then a liquid is formed which has the properties of ionic liquids but is readily volatile at low temperatures and can be distilled [13]. Typically electrochemical measurements in this class of IL is performed using silver wire quasi-reference electrodes separated from the electroactive species via a salt bridge [13, 14, 104–106]. Potential calibration is then performed using either cobaltocene or decamethylferrocene. The formal potentials of Cc and Fc in a variety of dILs are shown in Table 7.10. Ferrocene is not used in calibration of the quasi-reference electrode in DIMCARB as it has been shown to react with the dIL components.

Table 7.10 Formal potentials of $Cc^+|Cc^0$ and $Fc^+|Fc^0$ in distillable ionic liquids against an $Ag|Ag^+$ quasi-reference electrode

Distillable ionic liquid	$E_c^{\ominus\prime}$ of Cc|Cc$^+$	$E_c^{\ominus\prime}$ of DmFc|DmFc$^+$	References
DIMCARB	−613	238	[14]
DIMCARB	−602	238	[13, 104]
DIECARB	−682	280	[14]
MEETCARB	−668	270	[14]
MEPRCARB	−666	284	[14]

7.4 Considerations for Constructing Reference Electrodes for Ionic Liquid/Molten Salt Electrochemical Measurements

As with the reference electrode configurations for molecular solvents, it is generally recommended that a separated/fritted reference half-cell be used in all reference electrode configurations for ionic liquids (see also Chap. 4). This separation ensures that, even in the case of a quasi-reference electrode, the solution surrounding the metal wire will remain relatively constant, allowing a stable reference potential to be established. As minimal current will flow through this separate fritted half-cell, there will be minimal change in concentration in this half-cell solution. Ionic liquids tend to be much more viscous than molecular solvents such as acetonitrile or water. Consequently, wetting of the frit of the reference electrode half-cell with IL can be slow in the case of the commonly used Vycor® tip and may take over 24 h when starting from a dry state. In contrast, ultrafine porous glass frits can wet in <10 min. This feature may lead to the recommendation of the use of such frits when using ionic liquids [24]. However, the risk of contamination and leaking of solution to the working compartment of the cell is much greater than with Vycor® tips. On balance, the Vycor® tip is superior, as once it is wetted, refreshing of the reference half-cell solution and re-wetting out of the Vycor® tip are relatively rapid.

As previously discussed in this chapter, the physical positioning of the working electrode and reference electrode to minimise the electrode separation and thus to minimise IR_u can be restrictive due to the physical size of the electrode, especially when using macrosized electrodes. For many working electrodes the inert electrode housing itself can be up to several millimetres thick which can impact upon the separation distance (see Fig. 7.3). If consideration is not given to the experimental set-up, it may be difficult to reduce the electrode separation sufficiently to avoid working in the infinite linear R_u region (see Fig. 7.4). Luggin capillaries can be used to alleviate this problem and ensure closer working electrode to reference electrode separation. Using a Luggin capillary, much closer positioning (within 1–5 mm) is possible. However, care needs to be taken to use a capillary that is small enough in diameter that it does not screen the electrode and block part of the current density flowing between the auxiliary and working electrodes.

Experimentally it is best to utilise the same ionic liquid within the reference electrode compartment as also used in the test solution or working electrode compartment. This ensures that junction potentials are kept to a minimum. As

geometry and configuration of the cell changes from experiment to experiment, it is possible for junction potentials to vary in unpredictable ways. Thus, it is best to minimise ΔE_j effects as far as practicable. Using the same ionic liquid can be restrictive when, for example, a range of ionic liquids are being investigated. However, in all instances, it is advisable to fully characterise the reference electrode of choice, using a reference compound (such as ferrocene or cobaltocinium). Often, this will need to be done before or after the experiment to ensure the reference electrode is functioning properly and to ensure that any electrode drift effects are taken into consideration when evaluating experimental data.

When operating at higher temperatures with ILs, the choice of reference electrode systems is limited as stated above. Hence, a suitable reference couple must be chosen which is stable over the temperature range of experimentation. Similar to the lower temperature versions, the reference electrode should be separated from the electroactive species by use of a salt bridge. The choice of frit material is crucial as conventional frits such as Vycor® can experience problems at elevated temperatures. However, glass frits should be stable for most applications. Prior to running measurements, it is important to allow sufficient time for the reference electrode and salt bridge to calibrate to the operating temperature. Ideally, the reference electrode should be calibrated to a suitable reference couple in order to allow accurate determination of potentials. The choice of reference couple will be dependent on the operating temperature. However, if metallocenes are used, the volatility of these should be checked prior to calibration.

In the case of PILs, choice of reference electrode is simplified. As shown in Sect. 7.3.5.1 the Ag|AgCl|KCl$_{(PIL)}$ reference electrode appears to be suitable for use and shows stable reference potentials. Alternatively, the H$_2$|H$^+$ reference electrode can be used; however, care should be taken when using H$_2$ gas. Since well defined reference systems are available the use of quasi-reference electrodes is not recommended. For Lewis acidic ILs the Al|Al^{3+} reference electrode has been shown to be suitable for use in a large variety of systems; hence, it is recommended that this reference electrode be used as a standard.

In molten salt electrochemistry all reference electrodes face similar issues due to the elevated temperatures of operation. Mostly, this is due to the type of electrode casing materials used for construction of the reference electrode. Thus, for molten salts operated between 450 and 600 °C, sodium glass (or pyrex) can be sufficient as the electrode housing (encasing) [9]. This is easily fabricated into thin walled (ion conducting) junctions, using conventional glass blowing techniques. However, due to the melting temperature of 820 °C, the use is precluded above around 600 °C due to softening and deformation of the glass. Ionic conduction through the glass membrane is typically achieved with the sodium ion content in the glass.

For higher temperature applications (up to 1,200 °C), quartz is commonly used, which begins to soften at around 1,400 °C. However, as was seen with the Ag|AgCl reference for chloride melts employed by Gao et al. [68], the lower temperature use (below 700 °C) was limited due to the high impedance (~4 × 10^5 Ω) of the reference electrode. The thickness of the end-wall is such that insufficient ionic conduction at temperatures below 750 °C is common. The majority of potentiostats

Fig. 7.10 Tungsten tip
junction for molten salt
reference electrodes
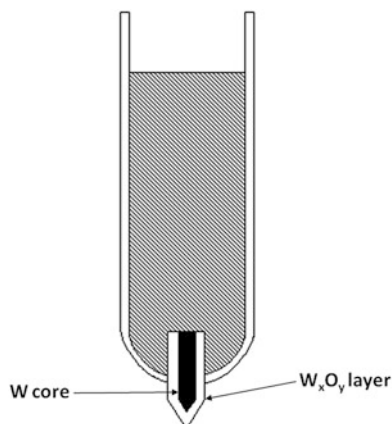
do not provide a stable response when high reference electrode impedance is
encountered resulting in extremely noisy voltammograms.

In work by Park et al. [69], it is suggested that a tungsten tip junction, which
contains a porous metal oxide layer for ionic conduction, can overcome this
problem at temperatures between 450 and 600 °C. A schematic of this reference
electrode junction is shown in Fig. 7.10. Here the tungsten wire which is embedded
in the quartz tube is oxidised to tungsten oxide. The tungsten oxide is much more
porous (with a density of 7.16 g cm^{-3}) compared to the tungsten metal (with a
density of 19.35 g cm^{-3}). Consequently, the tungsten oxide layer (formed in the
melt) allows an ionic conduction pathway for ions across the reference electrode
liquid junction. In electrochemical measurements in which the stability over time of
this type of reference electrode casing was measured, it was found that these
electrodes were stable at 700 °C for over 12 h [69].

For work in fluoride melts, such as cryolite [82] and LiF–NaF–KF (FLINAK)
[80], boron nitride has been suggested as a reference electrode containment mate-
rial. In work by Kontoyannis et al. [80], pyrolytic boron nitride is slowly
impregnated by the melt to provide ionic contact. Boron nitride has a resistivity
of about 2.3×10^{10} Ω cm at 500 °C [78]. However, it becomes ionically conduc-
tive as it is impregnated with the molten salt, thus providing good ionic contact
between the two half-cells while limiting diffusion between them. This encasing
was used successfully between 500 and 550 °C [80]. At higher temperatures the BN
tends to degrade and mixes into the melt. Also, boric oxide binders used in the tube
will dissolve and change the electrode potential via contamination of the melt. In
this same work [80], it is suggested that a boron nitride-coated graphite container is
used as the reference compartment. The bottom is left free with the rest of the
container electrically insulated by the boron nitride.

Finally, in the past [107, 108], a sodium ion conducting porcelain reference
electrode casing has been suggested. These can be used to much higher
temperatures than glass (1,000 °C) and was typically composed of 2.5 % Na$_2$O,

73.1 % SiO_2 and 24.4 % Al_2O_3 by weight. A major problem with these types of casings is the durability; they are quite fragile.

7.5 Conclusions

As has been shown in the preceding sections, there is no universal reference electrode system which works for all kinds of molten salts or ionic liquid electrochemistry. Indeed the reference electrodes that can be used are dependent upon the solvent system. Consequently, careful consideration should be made for choice of reference electrode and thought given to its use within the solvent system under investigation.

Prior to use of any reference electrode system for molten salts or ionic liquids, the electrode must be characterised fully in the solvent and calibrated. The reference electrode selection criteria are the same as found for non-aqueous electrodes (see Chaps. 3 and 6), and the final choice of reference system must also follow those guidelines of stability with time (no drift in potential) and temperature (stable over the operating range to be used), and it should be reproducible and convenient to use. In the case of ionic liquids, much work still needs to be performed in order to fully characterise reference electrode systems that can be used.

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